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Gaseous Mixtures of Hydrogen Chloride  
and Water on Aluminum Oxide and  
Application to Solid-Propellant  
Rocket Exhaust Clouds

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and Space Administration

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## SUMMARY

Significant quantities of hydrogen chloride (HCl) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) are exhaust products of large aluminized solid-propellant rocket motors (SRM). Understanding the interaction of the HCl/ $\text{H}_2\text{O}$ / $\text{Al}_2\text{O}_3$  system, applied to the SRM cloud, is important in assessing potential environmental impacts of SRM launches. Therefore, a study of the sorption of gaseous mixtures of HCl and  $\text{H}_2\text{O}$  on aluminum oxide was undertaken.

Samples of alumina (prepared from calcination of aluminum hydroxide) were exposed to a continuously flowing mixture of gaseous HCl/ $\text{H}_2\text{O}$  (35 to 300 ppm HCl at 75 percent of vapor composition at vapor/liquid saturation) in nitrogen ( $\text{N}_2$ ) at ambient temperature and pressure. A microbalance was employed to measure weight gains (or losses) which were recorded throughout sorption histories.

Maximum sorption capacity at steady state (typically requiring approximately 20 hours of exposure) was predominately controlled by specific surface area for samples of alpha, theta, and gamma alumina. Transient sorption rates for approximately 1-mg samples were characterized linearly with an empirical relationship that accounted for particle specific surface area and logarithmic time.

Chemisorption (weight gain retained after desorption into dry  $\text{N}_2$ ) of gaseous HCl and  $\text{H}_2\text{O}$  was found to occur on all aluminas studied. The chemisorbed phase was predominately water soluble with respect to chloride and appeared to form from about a mole ratio for HCl to  $\text{H}_2\text{O}$  of 2/5. Mole ratios of about 3.3/1 were obtained for soluble chloride to aluminum III, suggesting that substantial chloride dissolved as an aluminum salt.

Results from isopiestic experiments in aqueous hydrochloric acid solutions indicated that dissolution of alumina led to an increase in the vapor pressure of water over the solutions.

The results suggest that  $\text{H}_2\text{O}$  soluble aluminum salts (chlorides and/or oxy-chlorides) will form on the surface of SRM alumina as a result of gas-solid  $\text{H}_2\text{O}$ /HCl/ $\text{Al}_2\text{O}_3$  reactions in the exhaust cloud. The rate of formation of these salts appears to be strongly influenced by the surface area of the particulate alumina.

If condensation of gaseous HCl and  $\text{H}_2\text{O}$  forms an aqueous acid phase on SRM alumina particulates, dissolution of the "chlorided" phase may result, exposing previously unreacted surface for additional dissolution reactions. Solvated aluminum species will increase the vapor pressure of water and tend to promote evaporation of aqueous aerosol. Thus, a significant potential exists for HCl/ $\text{H}_2\text{O}$ / $\text{Al}_2\text{O}_3$  interactions to alter SRM aerosol nucleation/condensation/evaporation dynamics.

## INTRODUCTION

Large aluminized solid-propellant rocket motors (SRM) produce significant quantities of hydrogen chloride (HCl) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) as exhaust product effluents (ref. 1). The consequent impact of these products on the environment is being examined by the National Aeronautics and Space Administration. A major objective of these efforts is the development of accurate analytical models to predict dispersion and chemical reaction of exhaust species in time and space and assess potential effects on the environment and, in particular, on ground receivers (e.g., foliage). At the present time, the primary models (ref. 2) almost exclusively consider meteorological parameters for predicting atmospheric dispersion of nonreactive SRM clouds and do not yet include much of the complex species chemistry.

The purpose of this paper is to examine some of the chemistry of the HCl/ $\text{H}_2\text{O}$ / $\text{Al}_2\text{O}_3$  system as it applies to the exhaust cloud and to determine the probable magnitude and effect of HCl/ $\text{H}_2\text{O}$  adsorption with subsequent reaction on  $\text{Al}_2\text{O}_3$  particles on the SRM exhaust cloud composition. This information can then, hopefully, provide guidance in future modeling of the essential cloud microphysics, specification of measurement requirements for model validation efforts, and interpretation of measurement results. It is also the intent of this paper to consider some of the likely chemical properties of the HCl-modified alumina particles and how these particles might then interact with the environment. The chemical nature of the chlorided surface, for example, may be of significance when potential effects on ground receivers are considered.

Aluminum oxide from rocket exhaust has previously been shown to consist of at least two crystalline phases, gamma and alpha (refs. 3 and 4), with the bulk of the particles falling in the 0.05- to 0.3- $\mu\text{m}$  range (refs. 5 and 6). The sorptive properties of these crystalline phases have been summarized extensively by Bailey and Wightman (ref. 7) who have investigated the sorption of the pure adsorbates (HCl and  $\text{H}_2\text{O}$ ) separately on both alumina varieties. They found that water-vapor adsorption on both aluminas involved only physisorption, whereas hydrogen chloride sorption involved a chemisorption process and was approximately 60 percent irreversible. Interestingly, they found that alpha alumina adsorbed more HCl and  $\text{H}_2\text{O}$  vapor per unit area than gamma, a transition alumina.

Since HCl and  $\text{H}_2\text{O}$  are both available in a tropospheric SRM exhaust cloud, this work attempts to characterize the simultaneous sorption of HCl and  $\text{H}_2\text{O}$  on alumina at ambient temperatures and pressures.

A gravimetric sorption technique (weight gain proportional to extent of sorption) was employed in this study. Aluminum oxide samples were deposited on a weighing pan suspended from a balance and exposed to a continuous flow of adsorbate. Since rate data on HCl/ $\text{H}_2\text{O}$  sorption were desired in addition to equilibrated values, a continuously recording system was utilized. The measurements were conducted with nitrogen ( $\text{N}_2$ ) diluent at room temperatures and pressures, physically relevant to tropospheric conditions.

# SYMBOLS

A	BET measured particulate specific surface area, $\text{m}^2/\text{g}$
B	constant in equation (3), $10^{-4} \text{ m}^4/\text{g}^2$
K	constant in equation (3), $0.09 \text{ g}/\text{m}^2$
t	time, min (t must be $>1$ min)
$t_0$	reference time, 1 min
$W_0$	initial weight of sample under consideration, g
$\Delta W$	change in weight, g
$\Delta W_{Cl}$	chemisorbed weight gain from chloride, g
$\Delta W_p$	total chemisorbed weight gain, g
X	mole fraction

## EXPERIMENTAL PROCEDURE

### Sample Preparations

Samples of alumina were prepared as described by Bielański and Sedzimir for their preparation I. (See ref. 8.) Basically,  $\text{Al}(\text{OH})_3$  was precipitated from  $\text{Al}(\text{NO}_3)_3$  solutions at room temperature with ammonia, washed and filtered, and then dried. Drying was done in a forced-air oven at  $150^\circ \text{C}$  rather than at room temperature. Material produced in this fashion was then calcined at appropriate temperatures to produce gamma, theta, or alpha alumina. The samples were analyzed by X-ray diffractometry to confirm crystalline variety.

TABLE 1.- CHARACTERIZATION OF ALUMINA PREPARATIONS

Preparation	Crystalline variety	Calcination temperature, $^\circ\text{C}$	Calcination time, hr	Surface area (BET), $\text{m}^2/\text{g}$
3	Gamma	700	7	92.9
4	Theta	900	7	91.8
6	Gamma	625	7	142
7	Alpha	1025	14	7.1
8	Mixture	500	6	300
9	Gamma	600	6	226.9

Preparation 8 was not identified as a particular crystalline variety since no clear diffraction pattern was observed. This material was probably highly amorphous and may have been a mixture of aluminum oxide and hydroxide-oxide. Preparation 9 alumina was prepared much later than the other preparations, and consequently, data from this preparation are limited. Surface areas (BET) were determined by low-temperature  $N_2$  adsorption (work by R. R. Bailey and J. P. Wightman at Virginia Polytechnic Institute and State University). The preparations of alumina used in this study are listed in table 1.

Some question may arise as to how representative the test aluminum oxides are of those produced by flame in an actual SRM exhaust plume. Metastable aluminum oxides (e.g., gamma) inherently contain small unspecified amounts of  $H_2O$  and/or OH when prepared by calcination. Low-temperature (less than  $700^\circ C$ ) calcination-produced alumina might be expected to contain a significantly higher  $H_2O$  and/or OH content than a flame-produced counterpart (as in a rocket exhaust); since calcination involves stripping of  $H_2O$  and OH (possibly creating micropores and submicropores), larger internal surface areas might also be anticipated. The aluminas produced by calcinations at higher temperatures generally have lower surface areas (some degree of "healing" and sintering probably occurs) and systematically lower hydroxyl ion contents.

The properties of flame-produced aluminas can vary also, however, and are not always well understood. Both gamma and alpha alumina particles can be converted to theta, for example, when passed through a hydrogen-oxygen torch (refs. 9 and 10). Initial particle sizes, temperature quenching rates, and availability and nature of contaminants are all thought to play significant roles in phase conversions or formations. Recently it has been demonstrated that formation of gamma alumina in a flame is strongly coupled to available  $H_2O$  and/or OH (ref. 11).

Currently much uncertainty exists about the nature of SRM-produced alumina. Generally, the large-diameter particles (greater than  $0.1 \mu m$ ) have been considered to be mostly alpha variety (refs. 4 and 5), and the small particles to be gamma, but these determinations are presently somewhat inconclusive. Suggestion of an alpha bulk phase with a surface coating of small submicrometer gamma particles has recently been made (ref. 4). Thus the definition and preparation of a representative alumina could be difficult, if not impossible, to achieve.

Although not really simulating SRM alumina, high-temperature calcination-produced aluminas are a logical and beneficial starting point from which useful observations can be made. If the chemistry is assumed to be essentially the same, it becomes a problem of degree rather than type. This assumption is used throughout this paper. A more comprehensive treatment of aluminum oxide can be found in references 7 and 10.

#### Gravimetric Measurements

An electronic microbalance, with both digital and strip-chart-recorder' read-out, was used exclusively for the gravimetric measurements, which were carried out in a flow system. Figure 1 shows a schematic of the experimental setup. The technique is described in subsequent paragraphs.

Samples of alumina were first dispersed in a closed vessel (using a blast of dry nitrogen) and were then allowed to settle uniformly over a 12-mm-diameter platinum weighing pan. Samples of alumina used in the experiments ranged from 1 to 12 mg (most about 1 mg) and all were deposited in the same fashion.

The loaded pan was quickly placed in the 1.1-liter exposure chamber and allowed to desorb into a continuous flow ( $300 \text{ cm}^3/\text{min}$ ) of high-purity nitrogen. After 3 hours (insuring a well-defined initial state for the alumina), the dry nitrogen flow was changed, by valving, typically to a  $\text{H}_2\text{O}/\text{HCl}/\text{N}_2$  mixture at atmospheric pressure and flowing at  $150 \text{ cm}^3/\text{min}$ . After valving to the adsorbate, a time lag of 4 to 6 min (probably corresponding to transit time from the bubbler through the lines and valves down into the chamber where the pan was suspended) was generally observed before the onset of weight gain. The onset of weight gain was chosen as the reference time "zero." All sorption measurements were conducted at room temperature, maintained between  $21^\circ$  and  $25^\circ \text{C}$ . Sample weight gains were then recorded continuously during the exposure cycle. Typically, after a predetermined amount of time or sorption, the flow was changed back to nitrogen and the samples were allowed to desorb.

#### Generation and Calibration of Gas Mixture

The  $\text{H}_2\text{O}/\text{HCl}/\text{N}_2$  gas mixtures were generated by passing  $150 \text{ cm}^3/\text{min}$  of  $\text{N}_2$  through a "source bubbler" containing an  $\text{HCl}/\text{H}_2\text{O}$  solution of known concentration. The  $\text{HCl}$  output concentrations generated from the source bubbler were experimentally measured by infrared absorption. The  $150\text{-cm}^3/\text{min}$  flow of  $\text{HCl}/\text{H}_2\text{O}/\text{N}_2$  gas was fed into an infrared absorption cell with a path length of 75 cm and a volume of  $2880 \text{ cm}^3$ . Significant time, therefore, was necessary for the  $150\text{-cm}^3/\text{min}$  flow to replace the volume of stagnant air in the cell, as well as to equilibrate with the cell walls. Thirty minutes were required after starting the flow to reach 79 percent of the maximum adsorption at steady state, with 60 minutes producing 97 percent of the steady-state absorption. The absorption measurements were made in the  $\text{HCl}$  P-branch ( $\text{P}(3)$  at  $3.54 \mu\text{m}$ ).

Source bubbler output concentrations were measured by infrared absorption and correlated with known gaseous concentrations of  $\text{HCl}/\text{N}_2$ , generated by continuously flow-blending precise volumes of  $\text{N}_2$  and  $\text{HCl}$ . Measurements down to below 50 ppm  $\text{HCl}$  could readily be verified with this system. The final results of these measurements indicated that the 6.04-, 5.03-, and 4.0-molar bubblers delivered, respectively, about 400, 105, and 45 ppm of  $\text{HCl}$  with a  $150\text{-cm}^3/\text{min}$  nitrogen throughput. These values correspond well with known equilibrium-vapor-pressure data of  $\text{HCl}$  over hydrochloric acid solutions (ref. 12).

The water-output concentrations, calculated from equilibrium data on the partial pressures of  $\text{H}_2\text{O}$  over  $\text{HCl}/\text{H}_2\text{O}$  solutions (ref. 7) should have been about 17 500, 21 000, and 24 000 ppm for the respective 6.04-, 5.03-, and 4.0-molar solutions. Gaseous water, for pure-water-sorption information, was generated in a fashion identical to that for the  $\text{HCl}/\text{H}_2\text{O}$  mixtures, except that the source bubbler was filled with distilled water. Water-output concentrations of about 27 700 ppm would be expected. No effort was undertaken to measure  $\text{H}_2\text{O}$  in the present work.

As previously indicated, the  $\text{H}_2\text{O}/\text{HCl}/\text{N}_2$  gas mixtures were fed into the exposure chamber at  $150\text{ cm}^3/\text{min}$ . An additional  $50\text{ cm}^3/\text{min}$  of dry nitrogen was fed through the sealed and pressure-tested balance head into the exposure chamber to prevent diffusion into the balance and attack of vital components. This  $50\text{-cm}^3/\text{min}$  flow was assumed to mix thoroughly with the  $150\text{-cm}^3/\text{min}$  flow and resulted in a 0.75 dilution factor for the final average chamber concentrations, calculated to be 300 ppm HCl (6.04 M), 79 ppm HCl (5.03 M), and 34 ppm HCl (4.0 M) for the indicated source-bubbler solutions. The chamber concentrations for water would also be 75 percent of the respective source-bubbler output.

#### Empty-Pan Weight Gains

The empty platinum pan exhibited about 0.01, 0.015, and 0.012 mg of adsorption at near-equilibrium when exposed to the  $\text{H}_2\text{O}/\text{HCl}/\text{N}_2$  effluent from the 6.04-, 5.03-, and 4.0-molar source bubblers, respectively. Steady-state adsorptions of 0.03 to 0.04 mg of  $\text{H}_2\text{O}$  at 75 percent saturation were obtained. Daily temperature variations may have accounted for the lack of a clear trend in these  $\text{HCl}/\text{H}_2\text{O}$  adsorptions as well as the range of values in the pure-water sorptions; however, daily noise levels experienced with the microbalance were about  $\pm 2\text{ }\mu\text{g}$ . This weight gain was completely reversible and when the  $\text{HCl}/\text{H}_2\text{O}/\text{N}_2$  mixture or  $\text{H}_2\text{O}/\text{N}_2$  mixture was changed to nitrogen by valving, the pan quickly returned to its initial weight. The pan weight gain was insignificant in most cases, and corrections only became crucial for light initial sample weights (less than 1 mg) during the first hour of weight gain, or for very unreactive samples (low surface area) such as the alpha alumina.

#### Simultaneous Use of Secondary Samples

A number of secondary  $\text{Al}_2\text{O}_3$  samples, contained in an identical platinum weighing pan (fig. 1) and closely matched in weight (within 0.1 mg) to the primary sample, were run simultaneously. These samples could be rapidly decoupled from the system during a run for chemical analysis, without undergoing a typical nitrogen desorption cycle. In this manner, the primary sample could be desorbed in a normal fashion for the consequent analysis of chemisorbed species, whereas the secondary sample (quickly decoupled) permitted analysis closely reflecting the total sorption concentrations and thus provided a method for comparison between reversible and nonreversible species concentrations.

#### Chemical Analysis of Samples

Species analysis after sorptions on both primary and secondary alumina samples was accomplished by using a water-quench technique. The samples were deposited in 20 ml of distilled water and agitated; then a suitable portion was titrated potentiometrically ( $\text{Cl}^-$  specific electrode) with silver ion to determine soluble chloride. The remaining portion was then filtered and analyzed either for soluble  $\text{Al}^{3+}$  by atomic adsorption or colorimetrically by method C of reference 13, depending upon the anticipated concentrations. To test the water-quench technique, solutions of  $\text{Al}_2\text{O}_3/\text{HCl}/\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3/\text{AlCl}_3/\text{H}_2\text{O}$  of known initial concentrations were prepared and monitored with time. A result of this

is shown in figure 2 which relates the pH behavior of a freshly prepared  $\text{Al}_2\text{O}_3/\text{HCl}/\text{H}_2\text{O}$  solution with time. Even though the solution pH changed significantly with time (indicating chemical reaction), periodic chloride analysis over 2 days revealed a constant chloride concentration which was equal to the original chloride concentration. This demonstration applied to all samples except those from preparation 8. However, subsequent tests indicated that all chloride could be quantitatively recovered from preparation 8 alumina by acidifying the water/chlorided-alumina suspension with  $\text{HNO}_3$  to a pH slightly less than 1, and retitrating for chloride. Similarly, actual water-quenched samples of alumina (except preparation 8) revealed no increase in  $\text{Cl}^-$  with  $\text{HNO}_3$  acidification. The water-quench technique thus was determined to be adequate as performed, with acidification necessary only with preparation 8 samples.

#### Measurement of Mass-Transfer Rates

A set of mass-transfer experiments were conducted to determine whether gas-phase transport of  $\text{HCl}/\text{H}_2\text{O}$  mixtures to sample surfaces was influencing (limiting) sorption rate behavior. Several pieces of filter paper pretreated with  $\text{NaOH}$  solution were carefully trimmed, fitted to the weighing pan, and wetted with 50  $\mu\text{l}$  of 10-molar  $\text{NaOH}$  solution. Sodium-hydroxide-wetted filter paper was considered to be an excellent capturing medium for  $\text{H}_2\text{O}$  in the  $\text{HCl}/\text{H}_2\text{O}$  gas mixtures and, in particular, a "perfect" sink for  $\text{HCl}$ . Results from this series of tests (5-molar source bubbler) are shown in figure 3 for both total  $\text{HCl} + \text{H}_2\text{O}$  and chloride mass transfer. The error bars represent maximum spread encountered among five individual runs at each time. Significantly, no  $\text{Al}_2\text{O}_3$  microbalance runs were made with comparable mass accumulation rates. Chloride transfer was always at least a factor of 3 slower for preparation 8 samples, of 5 slower for preparation 6 samples, and of 7 slower for preparation 3 and 4 samples. Gas-phase convective diffusion to the external surface of the pan-supported alumina samples, therefore, was ruled out as rate determining in the sorption runs.

#### Isopiestic Vapor-Pressure Measurements

Isopiestic experiments were conducted to examine vapor-pressure behavior associated with  $\text{Al}_2\text{O}_3/\text{HCl}/\text{H}_2\text{O}$  solutions. A schematic of the apparatus can be seen in figure 4. A standard laboratory bell jar with 500 ml of 2.8-molar hydrochloric acid as a reservoir was used throughout the experiments. Small 20-ml glass sample vials and their contents were then placed on a glass rack over the reservoir solution, the jar was sealed, and the sample was allowed to equilibrate with the reservoir. The apparatus was maintained at  $30^\circ \pm 1.5^\circ \text{C}$  in a temperature-controlled oven. The temperature cycling in the oven was fast (period of 10 min), and fluctuations in the bell jar should have been considerably dampened. Mixtures of alumina and hydrochloric acid (initially 2.8 molar) or hydrochloric acid/aluminum chloride solutions of equal (2.8 molar) chloride molarity were placed in the sample vials. The  $\text{HCl}$  and  $\text{H}_2\text{O}$  partial pressures in the chamber were dominated by the large reservoir solution, and as a consequence, solutions in the sample vials adjusted composition to match partial pressures. With subsequent chemical analysis and weight gain/loss information, tendencies for evaporation or condensation were deduced relative to equilibration with reservoir solutions.

## RESULTS AND DISCUSSION

Figure 5 represents a typical HCl/H<sub>2</sub>O adsorption-reaction run on a large (11 mg) sample of preparation 3 gamma alumina. Almost all weight-gain histories for alumina samples exposed to HCl/H<sub>2</sub>O mixtures in the microbalance system displayed essentially the same characteristic features. Runs could be segmented into (1) an initial period of rapid weight gain during the early sorption history, (2) a period of deceleratory weight-gain behavior, (3) a region in which near-equilibrated weight gain is slowly approached asymptotically, and (4) a relatively rapid region of desorption under nitrogen displaying a residual weight gain.

### The Steady State

The amount of time necessary for an individual alumina sample to reach a near-equilibrated state was largely dependent upon the initial loading. Smaller initial loadings produced higher percentage weight gains per given period of time during early phases of the sorption history. This effect is demonstrated in figure 6 for different initial loadings of preparation 3, exposed to 300 ppm of HCl for 1/2 hour. The degree of particle bed formation would be anticipated to increase with the heavier initial loadings, and interparticle bed diffusion processes should therefore exert a progressively stronger influence on the rate of sample weight gain. Applying this reasoning, an attempt was made to run samples of minimum weight (thereby minimizing interparticle diffusion effects) that would more closely simulate the condition of particles suspended in an SRM exhaust cloud. Samples much smaller than 1.0 mg, however, were difficult to run on the microbalance since vibrational noise became a problem at the sensitivities necessary to record weight gains and correction factors for weight gain resulting from empty-pan adsorption became a more significant source of error. For these reasons, even though samples of approximately 0.25 mg were run successfully, the bulk of alumina runs were made with initial weight ranging between 0.5 to 1.5 mg.

Initial sample size, however, was never found to alter measurably the near-equilibrium sorption capacities in terms of percentage weight gain; each preparation of alumina appeared to have a prescribed capacity for water and hydrogen chloride over the concentration range of the experiments.

Particle specific surface area was found to primarily govern sorption capacity. The overall dominance of the specific surface area in the sorption process can be seen in figure 7. In this figure, both the percentages of weight gain at near-equilibrium and the chemisorbed weight gain after desorption are shown for samples weighing approximately 1 mg of alpha, theta, and gamma alumina exposed to 300, 79, and 34 ppm HCl. All data points represent the averaged weight gains of alumina samples (preparation numbers designated) exposed to each of the three HCl/H<sub>2</sub>O concentrations. The data from preparation 8 deviate somewhat from the apparent linear relationship with specific surface area. Although not supported by hard evidence, the initial BET N<sub>2</sub> measured specific surface areas are nearly linearly proportional to the sorption capacities for chemically similar samples of Al<sub>2</sub>O<sub>3</sub>. This proportionality, however, is altered when a mixed AlOOH/Al<sub>2</sub>O<sub>3</sub>,

which preparation 8 is considered to be, is introduced; consequently, preparation 8 deviates from the trend.

Near-equilibrium sorption results for  $H_2O/N_2$  and  $HCl/H_2O/N_2$  mixtures on the aluminas are summarized in table 2. Quantities of net weight gain (after pan correction) were anticipated to be at gravimetrically unresolvable levels for 75-percent-saturated water sorptions on preparation 7 alumina, and consequently no measurements were attempted.

TABLE 2.- REVERSIBLE AND IRREVERSIBLE SORPTION COVERAGES  
ON ALUMINA PREPARATIONS

(a) 75 percent  $H_2O$  saturation in  $N_2$

Preparation	Near-equilibrium sorption coverage		Chemisorption coverage	
	mg/g	mg/m <sup>2</sup>	mg/g	mg/m <sup>2</sup>
3	32	0.34	12	0.13
4	33	.36	11	.12
6	84	.59	30	.21
7	---	---	---	---
8	510	1.7	96	.32
9	173	.76	22	.097

(b) 75 percent  $HCl/H_2O$  saturation in  $N_2$

Preparation	Near-equilibrium sorption (a)		Chemisorption (a)	
	mg/g	mg/m <sup>2</sup>	mg/g	mg/m <sup>2</sup>
3	224	2.4	108	1.2
4	223	2.4	101	1.1
6	314	2.2	149	1.05
7	8.7 ± 1	1.2	5 ± 1	.7
8	970	3.2	470	1.6
9	515	2.2	254	1.1

<sup>a</sup>Results from 300, 79, and 34 ppm  $HCl$  exposure data averaged.

It is clear from these tables that significantly more weight is both sorbed and retained by the alumina samples exposed to 75-percent-saturated HCl/H<sub>2</sub>O vapor mixtures. This, when compared to the adsorptions on the empty platinum pan (nonreactive), which produced highest weight gains with 75-percent-saturated water vapor, emphasizes the importance of chemical reaction on the adsorption process.

The specific sorptions (mg/m<sup>2</sup>), both chemical and physical, for the alpha alumina (preparation 7) exposed to the HCl/H<sub>2</sub>O mixtures were somewhat lower than for the metastable aluminas; however, since the specific sorptions decreased only by a factor of about 2 while the specific area decreased by more than an order of magnitude, the extent of sorption can still be generalized to be predominately controlled by particle surface area. Preparation 8, for reasons stated previously, might be anticipated to show enhanced reactivity as reflected in table 2(b). It must be concluded that aluminum oxide reactions with water and HCl over the concentration range of this study are largely controlled by the specific surface area of the particles.

#### Composition of Chemisorbed Phase

The composition and structural nature of the chemisorbed phase is probably very complicated, and was never completely identified. Peri (ref. 14) has pointed out that the chloride-alumina system can involve aluminum chlorides and oxychlorides, as well as substituted chloride for surface hydroxyl or oxide ions.

Although chemical analysis of the chemisorbed phase ultimately consisted of aqueous methods for chloride and aluminum III (see section entitled "Experimental Procedure"), it was initially unknown whether the chloride that reacted on the alumina (as HCl) would produce a water-soluble chloride product. A series of control experiments with varying HCl/H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> compositions demonstrated that samples from preparations 3, 4, 6, and 7 were chloride-conservative (that is, all chloride could be quantitatively accounted for as solvated chloride by titration with Ag<sup>+</sup> in aqueous solution without special treatment) for several days. This coupled with HNO<sub>3</sub> acidifications of actual water-quenched samples (revealing no gain in chloride over nonacidified samples) provided substantial, if not conclusive, evidence that chemical analysis for chlorine (as chloride) was quantitative as performed in these experiments. Sample preparation 8 was found to deviate somewhat from this behavior, requiring acidification; however, this is consistent with the pH-dependent equilibrium relationship between chloride and oxychlorides (particularly in the formation of large "polymeric" mixed cation/anion species) when the large "neutralizing" capacity of this preparation is considered.

Chlorine was found to account for about 45 percent of the total chemisorbed weight gain regardless of exposure times (greater than 1 hr), gas phase HCl/H<sub>2</sub>O concentrations, alumina variety,<sup>1</sup> or initial sample weight in nearly all experi-

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<sup>1</sup>Chloride analysis was not accomplished with the present procedure on small (approximately 1 mg) samples of alpha alumina (preparation 7).

ments. Since the only other potentially reactive gaseous component in the mixture was water, it was assumed to account for the rest of the weight gain.

The actual ratios of the mass of chemisorbed chloride to the mass of the chemisorbed phase, determined by titration of the chemisorbed phase in water for chloride, are shown in table 3.

TABLE 3.- RATIO OF MASS OF CHEMISORBED  $\text{Cl}^-$  TO MASS OF CHEMISORBED PHASE

Preparation	Mass ratio at near equilibrium for source-bubbler concentration of -			Mass ratio after 1 to 6 hr exposure to source-bubbler concentration of -		
	4 M	5 M (a)	6 M (a)	4 M (a)	5 M (a)	6 M (a)
3	---	0.42 (8)	0.40 (4)	---- ---	0.38 (4)	0.39 (2)
4	---	.44 (4)	.46 (2)	---- ---	.48 (4)	.48 (2)
6	---	.43 (2)	.45 (1)	0.55 (1)	---- ---	.46 (4)
7	---	---- ---	---- ---	---- ---	---- ---	---- ---
8	---	---- ---	.51 (1)	---- ---	.46 (4)	.58 (1)

<sup>a</sup>Number of samples analyzed is indicated in parentheses.

These results indicate that the composition of the chemisorbed phase may be relatively invariant with exposure time; that is, composition at times early (1 to 6 hr) in the sorption history may be very similar to the composition (though not the absolute amount) existing at near-equilibrium. This provides further evidence that the extent of sorption is coupled to the extent of chemical reaction.

The data in table 3 indicate that approximately 45 percent of the chemisorbed weight gain can be attributed to chloride. Since the mass of the hydrogen chloride molecule is about twice that of a water molecule, the chemisorbed phase appears to form from the sorption of about 2.5 molecules of water per molecule of hydrogen chloride. The composition of the chemisorbed phase, however, cannot be specified from this information alone.

The correlation of water-soluble aluminum III ion with chloride ion was never totally achieved in a fashion that would generate actual surface composition information. Both atomic adsorption and classical wet analysis for aluminum (typically on samples greater than 5 mg carried out to steady state) produced, when quenched, ratios of solvated chloride to aluminum III of 3.3 with a standard error of  $\pm 0.4$ . These results, of course, are very suggestive of aluminum chloride formation.

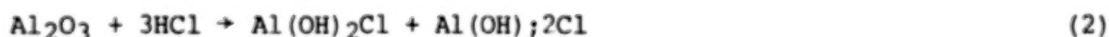
## Stoichiometric Consideration of Chemisorbed Phase

It seems reasonable to hypothesize that some water and/or hydroxyl groups, not observable as weight gain, would result from HCl attack of alumina. If, to simplify, it is assumed that the fraction of alumina undergoing chemical reaction reacts in stoichiometric "Al<sub>2</sub>O<sub>3</sub> block units" with no unreacted oxygens, variable amounts of hidden water and/or OH can result. For example, reaction of a block unit can produce a maximum of three water molecules as shown in the following equation:



No effort was made to hydrate the product in equation (1) since the present discussion is intended to focus on the production of H<sub>2</sub>O and/or OH.

A process in which attack of the block unit produces only hydroxyl ions is depicted in the reaction



Reactions (1) and (2) have been examined to demonstrate in a simple fashion that water and/or hydroxyl ions produced through HCl reactions can potentially mask apparent stoichiometries of chlorided alumina surfaces based solely on water weight-gain data.

On the other hand, the consequent hydration of such species would surely occur with the copious amounts of gaseous water available in the experiments. Thus, a hydration process could then be postulated to account for the experimentally measured weight gains attributed to water. The formation of hydrated ionic compounds is not inconsistent with the observed solubility in water of the chemisorbed phase. Water weight gains, however, appear too high to be explained with one simple stoichiometry involving ionic products. The potential exists for the chemisorbed phase to consist of a mixture of compounds, ranging in complexity from simple aluminum chloride hexahydrate  $[\text{Al}(\text{OH})_2]_6^{3+}; 3\text{Cl}^-]$  to extremely complicated aluminum oxychlorides  $[\text{Al}_x(\text{OH})_y(\text{OH})_z^{(3x-z)+}; (3x-z)\text{Cl}^-]$ .

## Composition of Reversible Phase

In order to determine the composition of the reversible phase at near-equilibrium, two very closely matched samples of aluminum oxide were exposed simultaneously to the same HCl/H<sub>2</sub>O bubbler effluent for a predetermined time. One sample was rapidly quenched in water before any N<sub>2</sub> desorption (see section "Experimental Procedure") while the other was allowed to desorb for 3 hours in typical fashion. An increase in chloride of only 4 percent was detected in the rapidly quenched sample. Four other similarly matched pairs produced results indicating chloride gains of  $4.0 \pm 0.92$  percent (standard error) when quenched, relative to their fully desorbed counterparts. Since the irreversible weight gain typically is about 50 percent of the total weight gain, the reversible portion of the sorption must consist of about 98 percent water by weight.

## Sorption Rates

A number of empirical approaches were tested in an effort to characterize the rate of uptake (sorption) of gaseous HCl/H<sub>2</sub>O mixtures by the alumina samples. Total sorption and chemisorption data on small samples (approximately 1 mg) were described best by an empirical log-of-time relationship. Data plots of percentage weight gain as a function of log of time usually supplied a reasonably good overall linear description of the rate behavior.

In figure 8, the relationship just discussed was applied to characterize the weight-gain histories of total sorption and chemisorption for preparation 8 samples. Six individual samples (ranging in initial weight between 1.09 and 0.93 mg) were needed since a desorption cycle was necessary at each time to obtain parallel chemisorption information.

A strong coupling between the kinetics of the sorption and chemisorption process is suggested by the apparent proportionality. These data (fig. 8) tend to reinforce earlier evidence that the extent of total sorption is controlled by surface reactions producing the chemisorbed phase. The reader should also recall the linear time relationship (nonlogarithmic) observed in the mass-transfer runs (fig. 3).

In figure 9 the linear log-of-time fit is shown for samples of preparations 3 and 4 exposed to three different gaseous HCl concentrations. The log-of-time fit can be seen to characterize the three HCl exposure concentrations adequately from 15 minutes to 12 hours. The relative insensitivity of the sorption process to HCl exposure concentration (34, 79, and 300 ppm) can also be observed in this figure.

In figure 10, the transition aluminas are shown to be describable by a linear log-of-time relationship from 15 minutes to 1 hour of exposure. The sorption depicted in figure 10(a) reveals accelerated weight-gain behavior when compared with the more typical sorptions on preparation 3 alumina shown in figure 9. Occasionally samples from each preparation would deviate more than the "normal"  $\pm 1$  percent weight-gain spread observed among individual samples, but the log-of-time relationship was almost always still followed. First-hour sorption behavior may be very relevant when applied to a continuously diluting SRM exhaust cloud, particularly if sorption rates are, as suggested by these data, somewhat insensitive to HCl concentration. The linear characterization, however, was not tested at concentrations of HCl less than 34 ppm. Preparation 7 alumina could not be utilized for kinetic measurements since overall weight gains for 1-mg samples on this low-surface-area alpha preparation were much too small for accurate measurements except at steady state.

Samples of alumina exposed to the 34 ppm HCl mixtures were generally not as well behaved during the early sorption history as were those exposed to the higher concentrations and frequently displayed some sort of early plateau. This effect can be seen in figure 11(a). The solid line represents the actual weight-gain history of a 1.09-mg sample of preparation 4 exposed to the 34 ppm HCl mixture. The plateauing effect seen in this figure typifies a large number of sample preparations exposed at the 34-ppm concentration level, and when observed

(in about half the experiments), was always found to occur during the first hour. Exactly what this leveling-off phenomenon might represent is unclear at this time, and it is disturbing that this effect was not seen consistently.

In figure 11(b), the sorption history depicted in figure 11(a) is shown as percent weight gain as a function of time on a log scale. The early-plateau effect can be seen to perturb the linear characterization for the first hour or so, but the fit appears to be adequate for data after 2 hr of exposure to the HCl mixture. It should be noted that the first hour or two would seem to be the most desirable period for an understanding of the sorption behavior of alumina for application to the SRM exhaust cloud problem.

Since specific particle surface area had been demonstrated to have a dominant effect on sorptive capacity (fig. 7), its influence on the rate process was examined. The following equation was found (after empirical analysis of the respective effects of surface area and time) to adequately characterize sorption rate behavior in these experiments:

$$\frac{100 \Delta W}{W_0} = \left( KA - \frac{A^2}{B} \right) \log \frac{t}{t_0} \quad (3)$$

Data from 31 runs are summarized and plotted in figure 12 in accordance with the empirical correlation (eq. (3)). A best-fit line passing through the origin is shown for  $K = 0.09 \text{ g/m}^2$ . The greatest deviation can be seen to occur at (1) exposure time  $\leq 30 \text{ min}$  (possibly due to exposure chamber equilibration that may have temporarily reduced effective gas-phase concentrations) or (2) times  $\geq 20 \text{ hr}$ . The asymptotic approach to equilibrated sorption cannot be accounted for by the present form of equation (3).

Equation (3) can be used for estimates related to the alumina/SRM cloud chemistry problem provided the following limitations and potential pitfalls are recognized:

(a) All samples of alumina investigated were calcination produced rather than flame produced as in an SRM exhaust cloud.

(b) All data were taken at 75 percent relative vapor saturation whereas actual SRM cloud saturations may be highly variable.

(c) Concentrations of HCl were constant during most of the exposure histories, unlike the dilution-produced HCl decay anticipated in an SRM cloud.

(d) Data were collected on approximately 1-mg samples of alumina. Consequently, some bed diffusion effects existed and actual sorption processes may be faster for freely suspended particles in an SRM aerosol.

While equation (3) can be used to predict percentage weight gain (total sorption) with respect to time, slight variations can be incorporated to give equations to predict permanent weight gain

$$\Delta W_P = \frac{0.5W_0}{100} \left( KA - \frac{A^2}{B} \right) \log \frac{t}{t_0} \quad (4)$$

and "chlorided" weight gain

$$\Delta W_{Cl} \approx \frac{0.25W_0}{100} \left( K_A - \frac{A^2}{B} \right) \log \frac{t}{t_0} \quad (5)$$

The reader should recall that the chemisorbed weight gain was consistently found to be about one-half of the total sorption. Likewise, about one-half of the chemisorbed weight gain was accounted for by chloride ions.

Specific surface area was found to exert a largely dominating effect on the water sorption process also. Sorption behavior for pure water 75 percent saturated in nitrogen on preparations 3, 4, and 6 aluminas can be seen in figure 13. Data from water runs, in general, when plotted as percent weight gain as a function of time on a log scale, were not as well behaved (linear) as their HCl/H<sub>2</sub>O counterparts. Water runs consistently reached steady state much faster, producing a more sharply defined near-equilibrium end point. However, both the total sorptions (g/m<sup>2</sup>) (table 2) and mass accumulation rates (g/min-cm<sup>2</sup>) were several times smaller when compared with HCl/H<sub>2</sub>O sorptions. Since the principal focus of this work was HCl/H<sub>2</sub>O sorption and modification of alumina, further water information is not reported in this paper.

#### ISOPIESTIC EQUILIBRIA

Perhaps of greater significance than the rates of sorption and total quantities of HCl and H<sub>2</sub>O scavenged by the alumina particles is the chemical nature of the modified alumina surface. Aqueous acid aerosol formation may be strongly linked to the surface chemistry of the modified alumina particulates. Furthermore, evaporative or growth processes on acid aerosols once formed may be significantly influenced by solvated species. For these reasons, some preliminary isopiestic experiments were conducted to examine vapor-pressure behavior associated with Al<sub>2</sub>O<sub>3</sub>/HCl/H<sub>2</sub>O solutions. It was assumed that dissolution of alumina in hydrochloric acid would yield essentially the same solvated species that would result from alumina dissolution in actual SRM acid aerosol droplets. The isopiestic data are presented in table 4 showing both the initial and final chloride molarities equilibrated with the 2.857-molar reservoir hydrochloric acid solution. The calculated equilibrium pressures for HCl and H<sub>2</sub>O in the chamber were 0.0089 and 27.6 torr (1 torr = 133 Pa), respectively. The grams of HCl and H<sub>2</sub>O transferred (shown in table) were calculated to produce the resultant molarities while conforming to the weight-gain data.

In figure 14, the results for 10- and 14-day equilibrations can be seen. The results are plotted as weight gain in grams per initial grams of solution as a function of mole fraction of alumina. This mole fraction is in no sense a true mole fraction since the total weight of alumina was treated as dissolved rather than partitioned between solution and suspension as all mixtures actually were. Significantly, the vial containing no alumina showed a small positive weight gain, an indication that thermal gradients slightly favored weight gains. All samples containing alumina produced equilibrated weight losses, suggesting that acid aerosols once formed around an alumina nucleus would tend to evaporate if contrasted with a similar inert nucleus. The same results expressed as water loss in grams per milliliter can be seen in figure 15(a).

TABLE 4.- ISOPIESTIC EXPERIMENTAL PARAMETERS

Al <sub>2</sub> O <sub>3</sub> , g	HCl, ml	Ratio of Al <sub>2</sub> O <sub>3</sub> to HCl, g/ml	Molarity		$\Delta W$ , g	Calculated $\Delta W$ , g, for -	
			Initial	Final		HCl	H <sub>2</sub> O
0.50	2.0	0.25	2.857	3.36	-0.152	0.016	-0.168
.50	3.0	.167	2.857	3.18	-.114	.02	-.134
.50	4.0	.125	2.857	2.90	-.089	-----	-.089
.50	5.0	.100	2.857	2.94	-.075	.008	-.083
.50	8.0	.063	2.857	2.88	-.058	.002	-.060
.00	6.0	.000	2.857	2.80	.018	-.0004	.018

AlCl <sub>3</sub> , ml	HCl, ml	AlCl <sub>3</sub> , percent HCl	Molarity		$\Delta W$ , g	Calculated $\Delta W$ , g, for -	
			Initial	Final		HCl	H <sub>2</sub> O
4.00	0.00	100	2.775	3.2	-0.427	0.01	-0.437
1.00	2.00	33	2.83	3.16	-.089	.024	-.112
1.00	4.00	20	2.84	2.94	-.041	.012	-.053

Volumes of hydrochloric acid and aluminum chloride solution, of nearly equal chloride molarity (2.8 M), were mixed and equilibrated with the reservoir HCl solution. Here, as with the Al<sub>2</sub>O<sub>3</sub>/HCl mixtures, the calculated water loss can be seen to increase with aluminum content. (See fig. 15(b).) These results appear to be in good agreement with the more recent direct vapor-pressure measurements of Tyree (ref. 15) who concluded that the vapor pressure of water over hydrochloric acid solutions increased with the addition of powdered alumina. The extent and rate were primarily dependent upon the crystalline alumina phase, the particle size, and the hydrochloric acid concentration. An isopiestic experiment, however, is an equilibrium measurement typically involving several days and is, therefore, of limited value when applied to SRM cloud assessments, but it defines upper limits and clearly demonstrates the need for vapor-pressure measurements over more appropriate time frames.

#### IMPLICATIONS TO SRM EXHAUST CHEMISTRY

If near-equilibrium chloride coverages obtained from this work are assumed to be good measures of maximum chloride uptake from sorption processes by particulate alumina, SRM-produced alumina will not likely be a significant sink for gaseous HCl in the "dry" aerosol case. For example, the SRM exhaust is typically about 30 percent Al<sub>2</sub>O<sub>3</sub> and 21 percent HCl by weight (ref. 1). Using 30 m<sup>2</sup>/g as representative of an upper bound for the surface area of SRM-exhaust alumina (equivalent to an SRM exhaust of 0.05- $\mu$ m-diameter spherical alumina particles), a near-equilibrium coverage of about 2 percent chloride by weight would be predicted for the alumina, which, translated to the SRM cloud, constitutes

less than a 3-percent HCl removal. Current assessments (refs. 5 and 6) place the bulk of the particles in the 0.08- to 0.3- $\mu$ m range. It can be seen, therefore, that extremely large surface areas of alumina (greater than predicted) are necessary for any significant quantity of HCl to be scavenged from the SRM exhaust under dry aerosol conditions.

Although the removal of gaseous HCl by SRM alumina in the dry case (aerosol without an aqueous phase) is suggested to be somewhat nominal (with respect to the amount of HCl scavenged from the exhaust cloud), the effects of this on the surface properties of the alumina particles demand closer attention.

If an alumina nucleus is postulated to be an initial nucleation/condensation site, then the surface properties of the particulate (e.g., hygroscopicity) may well play a significant role in aqueous aerosol formation, in particular, acid aerosol formation. For example, results of water sorptions at near-equilibrium (75 percent relative humidity) on aluminum oxide samples, when compared with their 75-percent-saturated HCl/H<sub>2</sub>O counterpart samples, consistently produced weight gains attributed to water which in most cases were smaller by more than a factor of 3. (See tables 2(a) and (b).) This observation suggests that the HCl-modified surface may produce alumina particles with a larger capacity for water. This apparent enhancement of hydrophilicity, however, will likely only exert influence on the H<sub>2</sub>O adsorption process during accumulation of the first several monolayers and should not be linked with dissolution behavior once a substantial aqueous acid aerosol phase has formed around alumina particles. The latter phase represents a regime in which aqueous solution chemistry, rather than particle surface properties, will largely influence aerosol behavior.

If an aqueous acid phase should form around an alumina nucleus, a likely result in the "young" SRM cloud at relative humidities greater than 80 percent (refs. 16 and 17), consequent dissolution of alumina could greatly influence aerosol behavior. Significantly more HCl is likely to react with transition aluminas if a liquid hydrochloric acid phase forms. Hydrochloric acid and alumina reactions in solution can furnish a sink for gaseous HCl in the aerosol droplet through conversions to chloride salts, and in this manner generate capacity for further droplet absorption of gaseous HCl.

Dissolution reactions produce the opposite effect, however, with respect to water. Results from these isopiestic experiments as well as more recent dynamic vapor-pressure measurements (ref. 15) indicate that solvated aluminum species resulting from reaction will produce an increased H<sub>2</sub>O vapor pressure over a concentrated acid aerosol droplet when compared to the idealized "nonreactive nucleus" case. The results further suggest that this evaporative tendency will increase with increased alumina dissolution. Since SRM acid aerosol droplets should be largely composed of water (relative to HCl), and the common ion effect should reduce the rate of HCl absorption by droplets, it is concluded that alumina dissolution will promote "net" evaporation and thereby tend to retard early acid aerosol growth. However, these considerations apply to acid aerosol growth/evaporative processes in the presence of significant gaseous HCl and must be distinguished from aerosols primarily composed of water (which can potentially form much later in the exhaust dilution history). In the latter case a soluble chloride phase would be anticipated to promote condensation of water relative to a nonreactive nucleus.

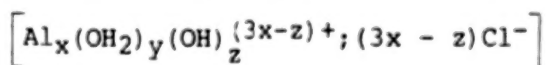
Since precipitation scavenging efficiencies are very strongly dependent on aerosol size distributions, the microchemical deviations from the idealized case (pure HCl/H<sub>2</sub>O aerosol on inert Al<sub>2</sub>O<sub>3</sub> particles) may have a significant effect on cloud microphysics and on acid rain predictions (refs. 18 to 20). Therefore, the use of vapor-pressure data for the pure HCl/H<sub>2</sub>O system for assessment of aerosol processes should include at least first-order corrections to account for alumina dissolution.

The major aluminum-containing ions resulting from dissolution cannot be specified for any given SRM/aerosol event, since they will be functions of temperature, time, individual species concentrations, and initial size and phase distribution of the alumina particles. Some comments are justified, however, and can serve as guidelines in a general sense.

Aluminum oxide dissolution can be viewed as an HCl neutralizing process in an acid aerosol droplet. For a very low pH to persist, there must be either a slight excess of HCl available over that required for total reaction with all the alumina or the reaction must be sufficiently slow "overall" so that alumina dissolution, and thereby neutralization, is slow. Although only 32 percent of the required acid is available to convert the total mass of SRM exhaust alumina to the trichloride, a significant portion (more than half) of the alumina will probably be of the alpha variety and, therefore, very slow in reacting with the HCl. The gamma fraction (or any metastable variety), however, is anticipated to dissolve more quickly in hydrochloric acid aerosol. Rapid dissolution of gamma alumina is supported by results of Dawbarn and Kinslow (ref. 4) obtained from their small SRM chamber firings.

Based on the preceding discussion, it is concluded that a significant amount of the acid aerosol formed early in the exhaust cloud history (air/exhaust ratios of less than 10<sup>5</sup>) will be likely to possess an environment acidic enough to form and maintain solvated aluminum chloride. Aluminum chloride hexahydrate  $[Al(OH_2)_6^{3+}; 3Cl^-]$  should remain the primary solvated aluminum species at a pH of 2 or less. It is suggested, therefore, that some effort should be made to examine the effects of aluminum chloride deposition on foliage, for example, since a large potential is considered to exist for its formation in the SRM exhaust cloud.

If, however, the acid content in a particular aerosol droplet is not sufficient to maintain a pH of less than 2, other aluminum species may result. The formation of generalized aluminum oxychlorides



is considered probable at a pH greater than 2. Lower acid content can result from aerosol formation later in the SRM cloud history or from acid loss in condensation/evaporation cycles.

While the properties of the solution species are important in aerosol chemistry, they can also be of major concern when considerations of potential ground-receiver damage mechanisms are considered. Aluminum oxychlorides are rather

innocuous compounds (in pure form), and their formation would be much preferred over aluminum chlorides from a toxicological (irritation) viewpoint (ref. 21).

Formation of (or conversion to) oxychloride, unfortunately, appears most likely to occur only after the SRM aerosol cloud has diluted greatly and, therefore, already becomes less of a local environmental problem. Oxychloride formation, however, may still be of importance when longer term impacts are considered.

#### CONCLUDING REMARKS

Experimental results on laboratory-prepared samples of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) have demonstrated that, in addition to physical adsorption, chemisorption of gaseous hydrogen chloride ( $\text{HCl}$ ) and  $\text{H}_2\text{O}$  mixtures occurred on the alumina at approximately  $23^\circ\text{C}$  and at atmospheric pressure. The chemisorbed phase appears to form from the sorption of about a 2.5 water-to-chloride mole ratio. The chemisorbed chloride phase, although not identified as a specific compound or structure, was found to be water soluble as a chloride. Solvated aluminum III ion was present in amounts ( $\text{Cl}^-/\text{Al}^{3+} = 3.3/1$  mole ratio) sufficient to suggest that the major portion of the chloride dissolved as an aluminum salt. These observations tend to support the formation of surface aluminum chlorides and/or oxychlorides during the sorption process.

Sorption rates were primarily found to depend on initial particle specific surface area and sample loading (bed thickness). The sorption rates on SRM exhaust cloud alumina (over the  $\text{HCl}/\text{H}_2\text{O}$  concentration range of this study) would not be expected to show any bed diffusion effects and, therefore, would be primarily governed by particle surface area. The near-equilibrated sorption capacities were linearly proportional to initial particle surface area. Rates of both chemisorption and total sorption were found to be proportional to the log of the exposure time at three different  $\text{HCl}/\text{H}_2\text{O}$  concentrations and on samples of differing surface area.

In conclusion, it is believed that the present results help to define some basic properties of  $\text{Al}_2\text{O}_3/\text{HCl}/\text{H}_2\text{O}$  interactions that can be used as a meaningful guide in anticipating the probable magnitudes and effects of  $\text{HCl}/\text{H}_2\text{O}$  sorption on alumina as it applies to an aluminized SRM exhaust cloud. The results help to place bounds on the likely properties of the modified alumina surface. The potential to alter aerosol nucleation/condensation/evaporation dynamics through vapor-pressure modification has been discussed, and some of the more probable solution species have been considered. The impact of all these potential modifications on the microchemistry and microphysics of the SRM  $\text{Al}_2\text{O}_3/\text{H}_2\text{O}/\text{HCl}$  system cannot be adequately integrated into a predictive scheme at this time. However, it is believed that some meaningful first-order approximations have been defined, along with some needs for future research efforts.

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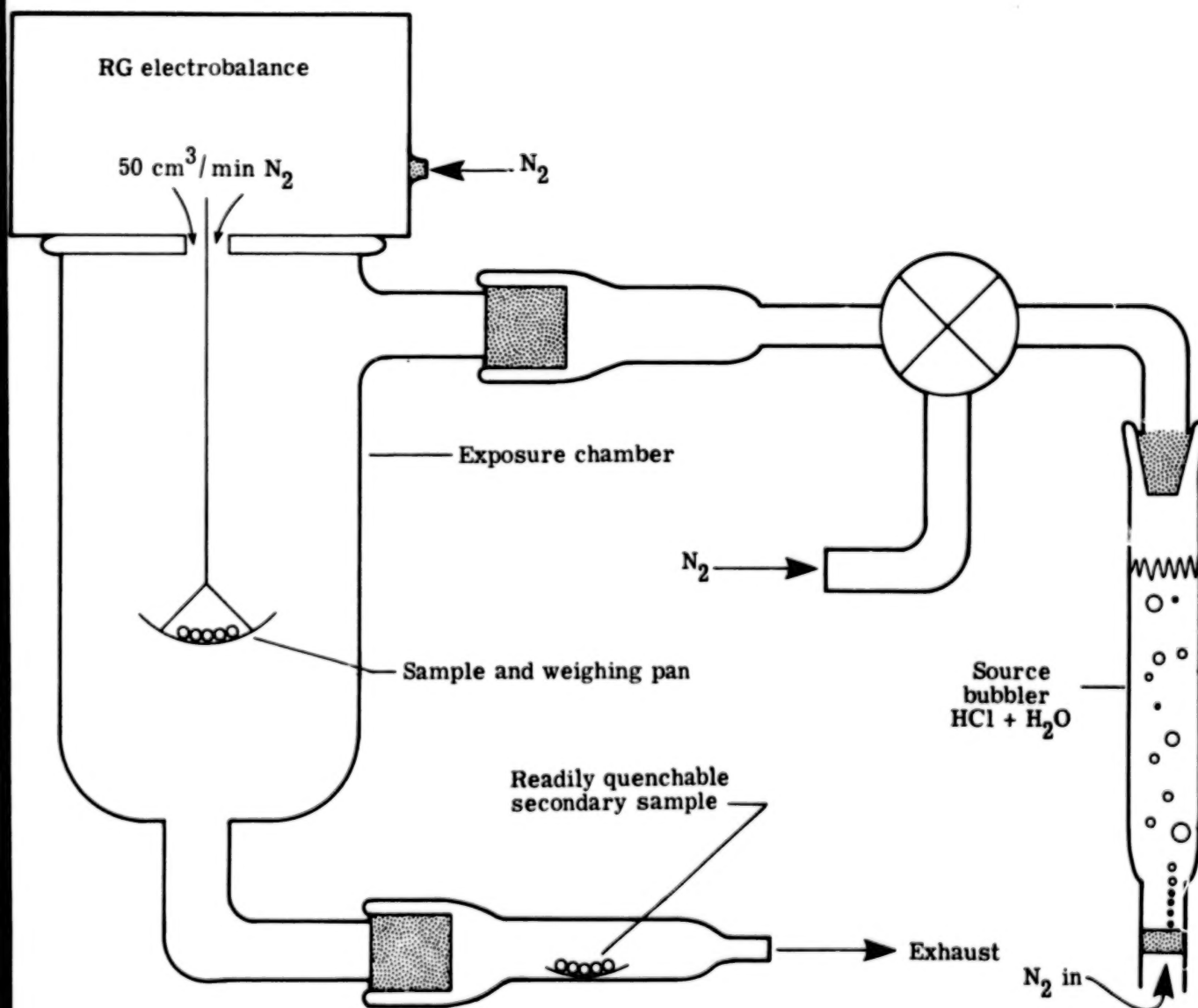


Figure 1.- Experimental apparatus for HCl/H<sub>2</sub>O sorption measurements.

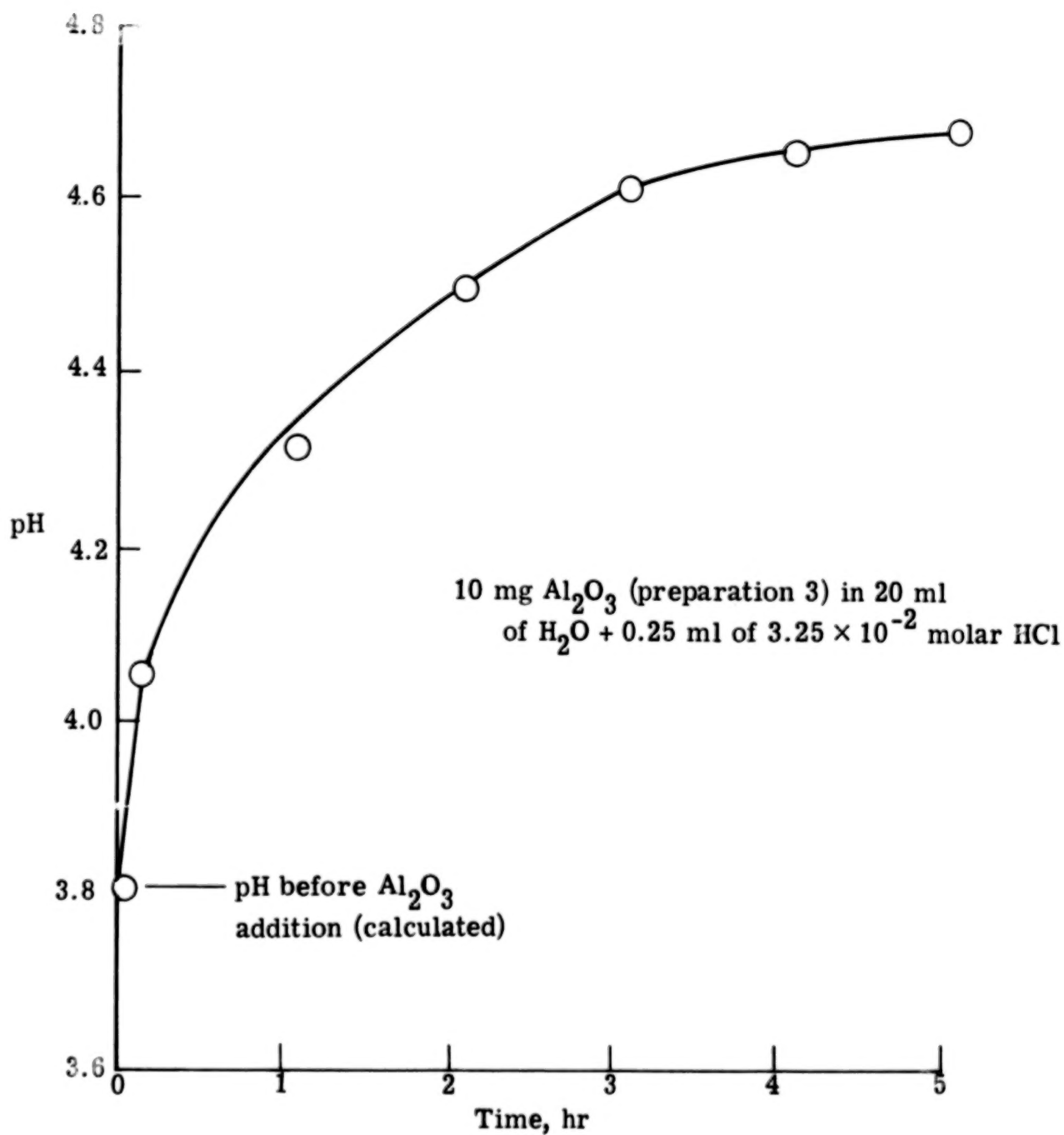


Figure 2.- pH behavior of hydrochloric acid solution after addition of alumina.

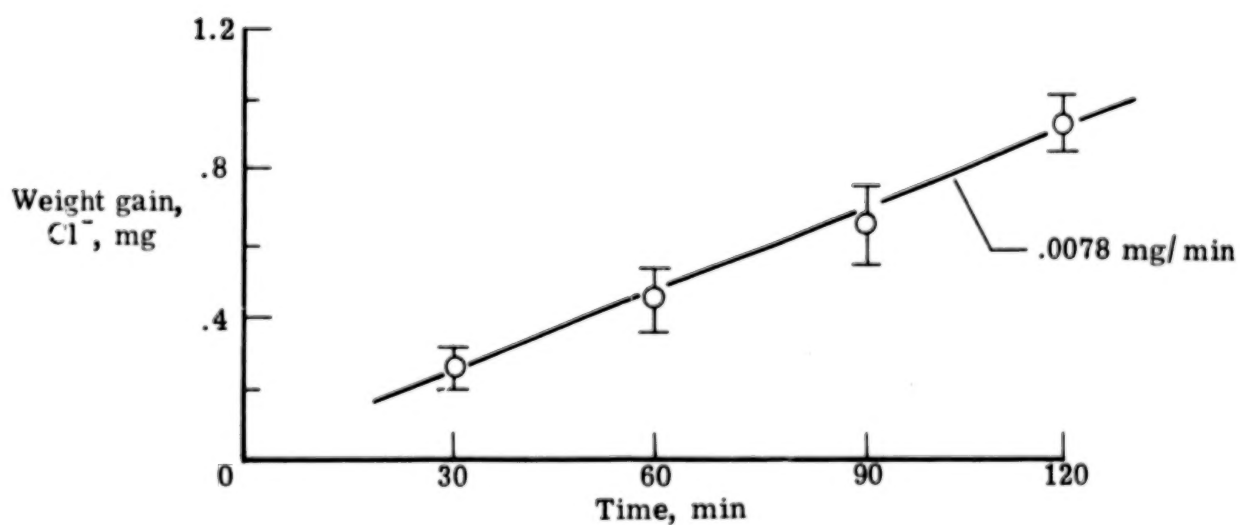
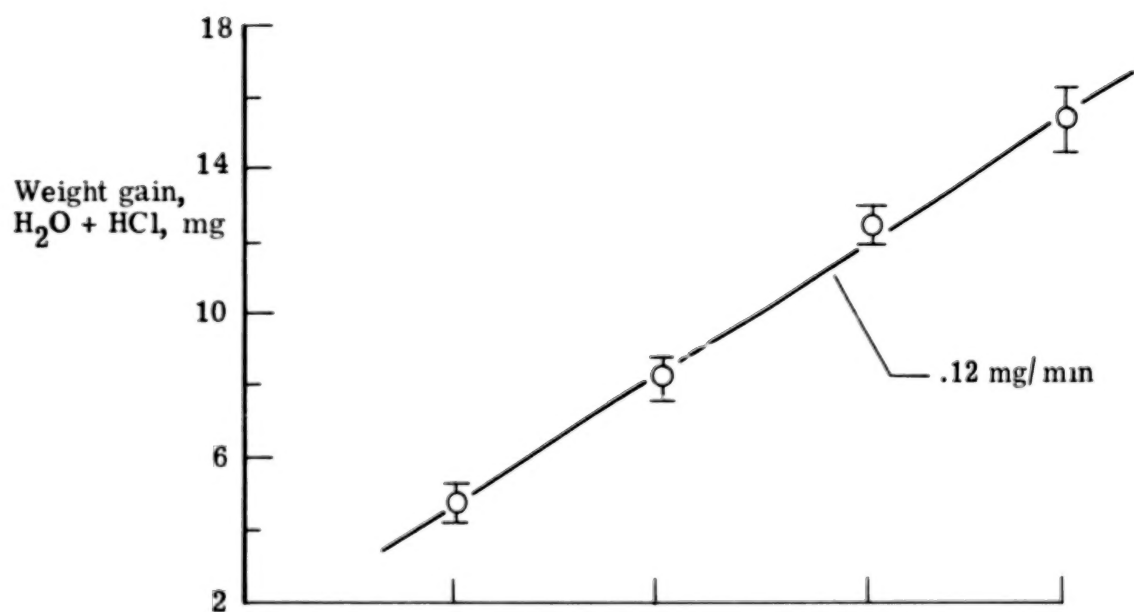


Figure 3.- Mass transfer of adsorbate to sodium-hydroxide-treated filter paper.

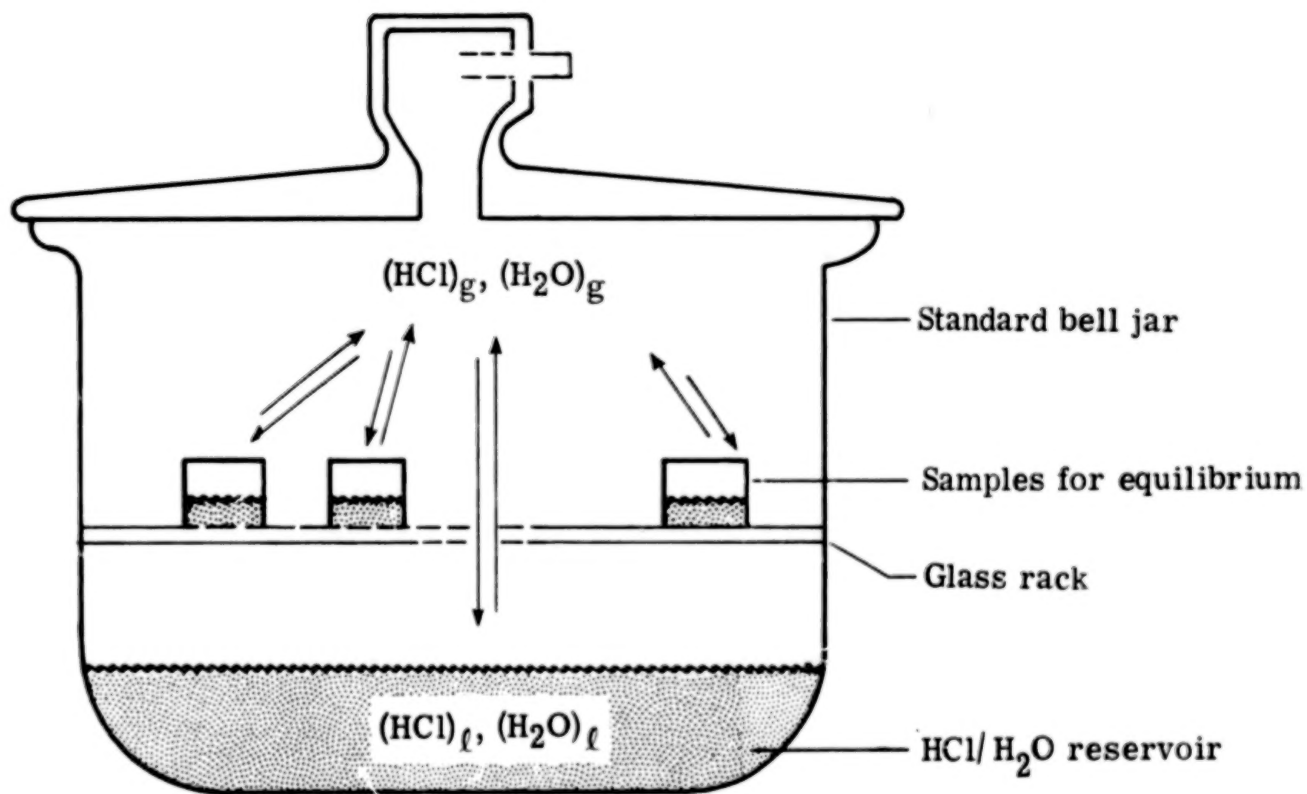


Figure 4.- Experimental apparatus for isopiestic measurements.

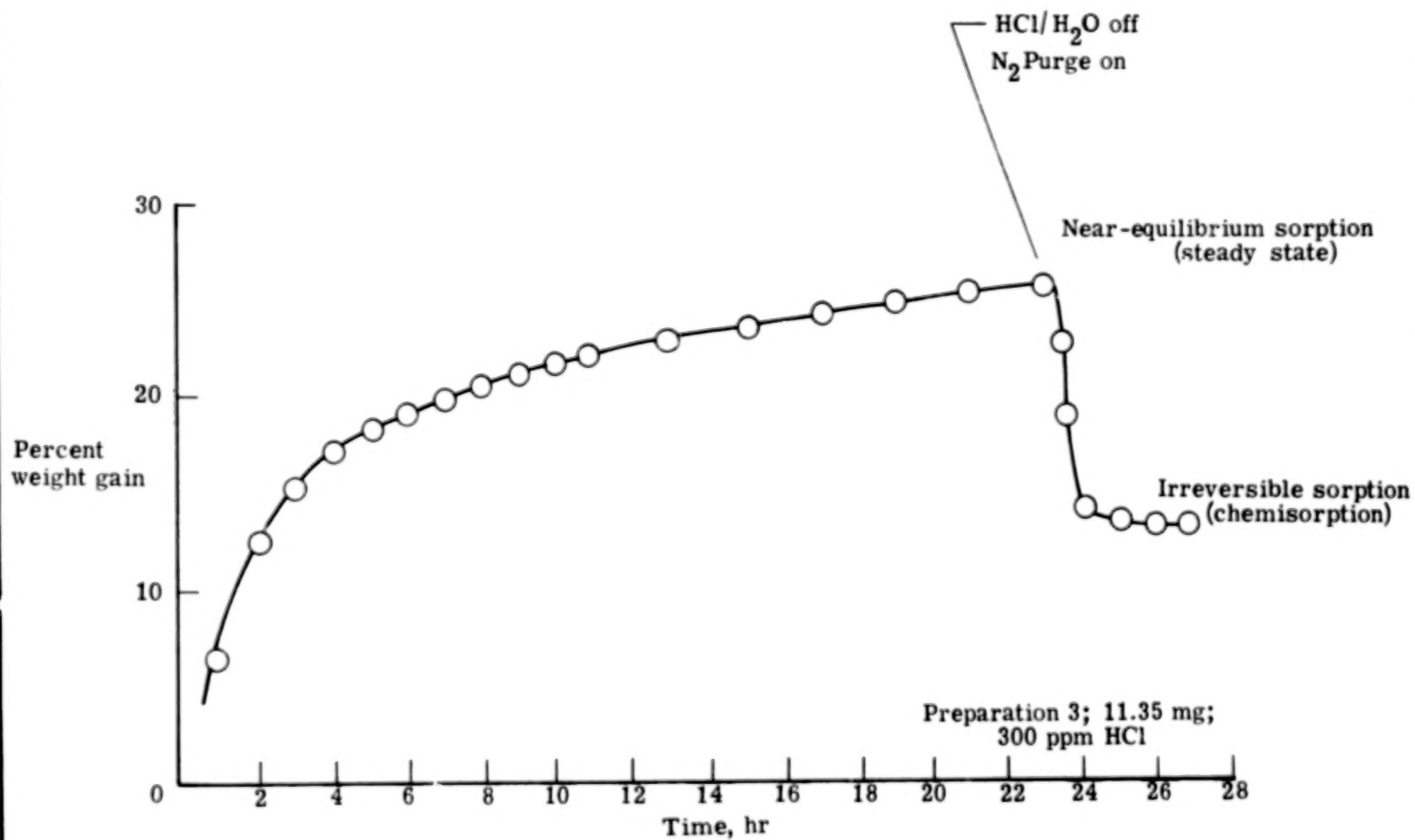


Figure 5.- Typical sorption history of gaseous HCl/H<sub>2</sub>O on alumina.

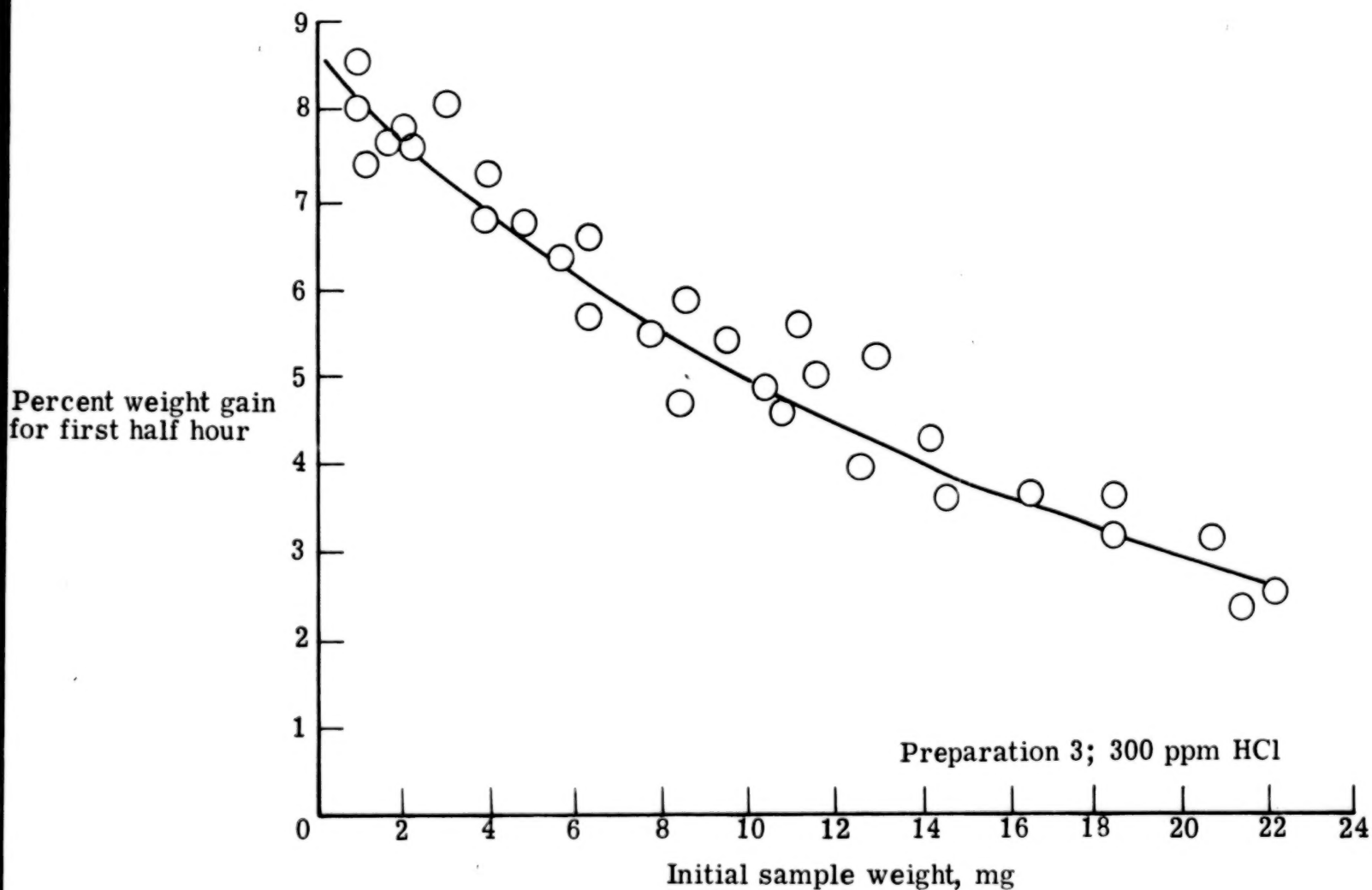


Figure 6.- Effect of initial  $\text{Al}_2\text{O}_3$  loading on first half-hour percent weight gain.

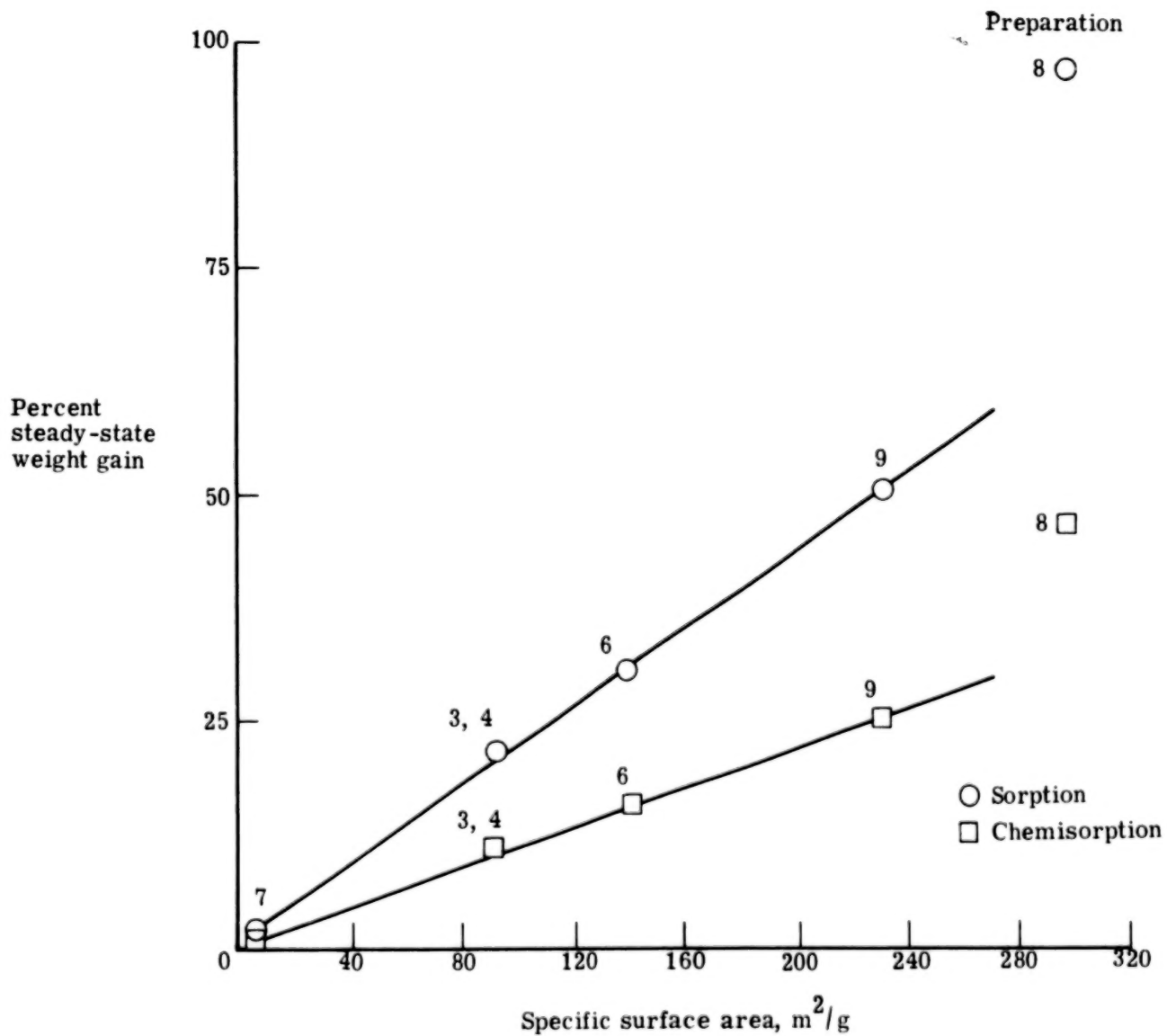


Figure 7.- Steady-state sorption capacity for specific surface area of alumina.

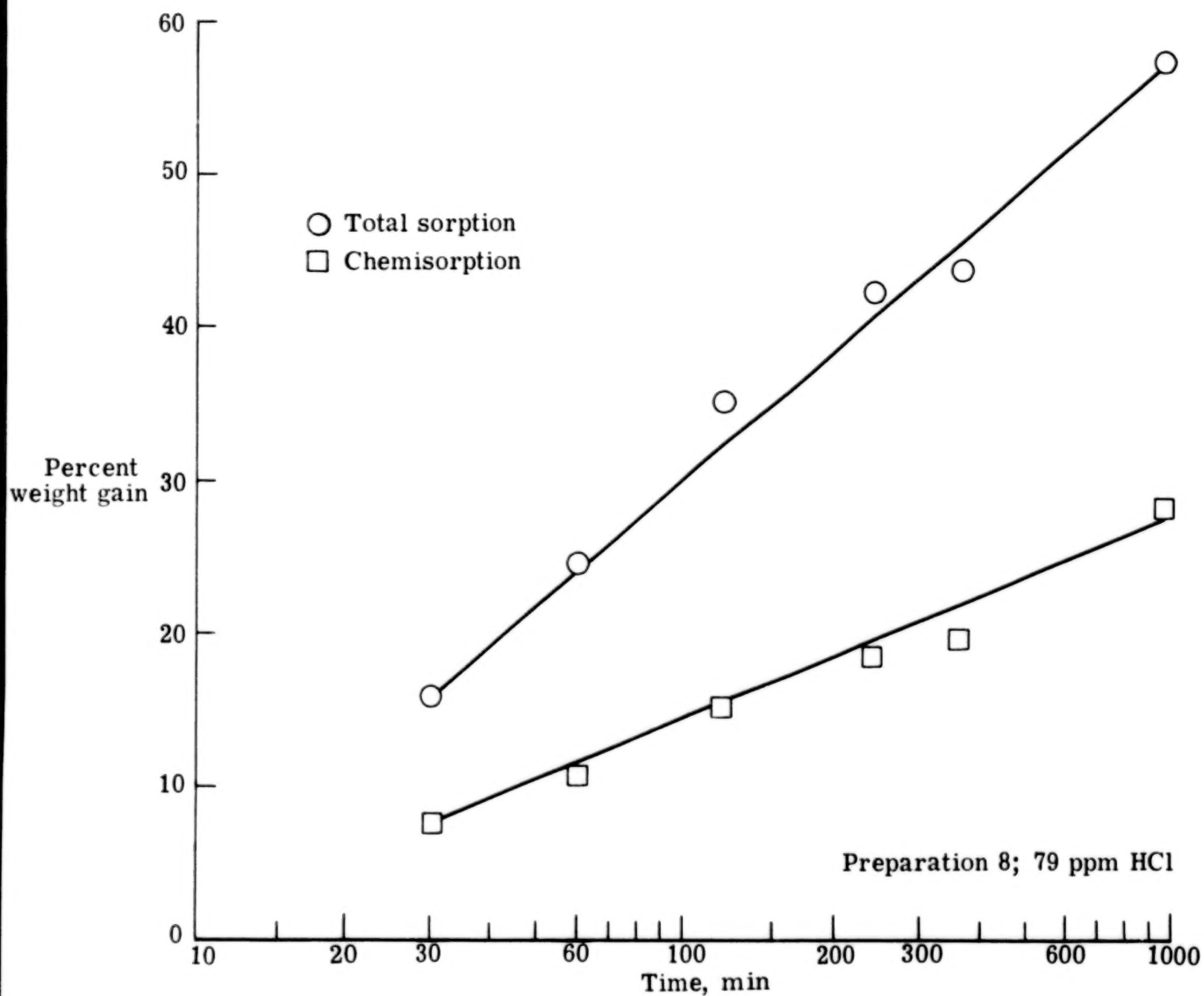


Figure 8.- Log-of-time fit for total sorption and chemisorption.

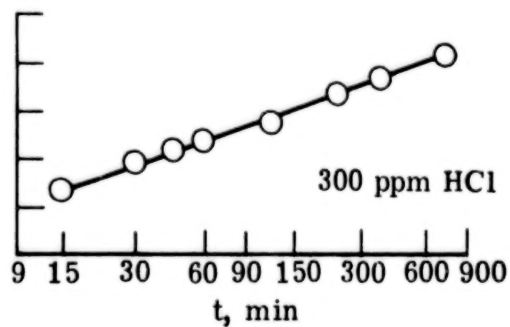
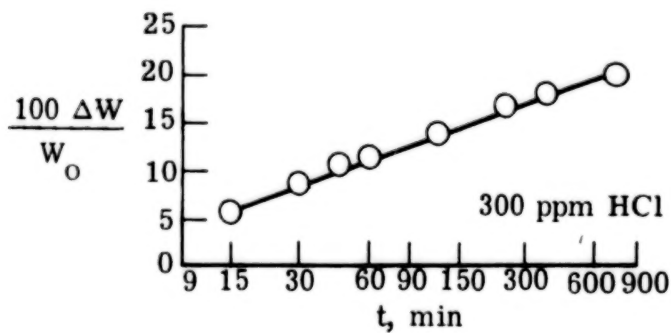
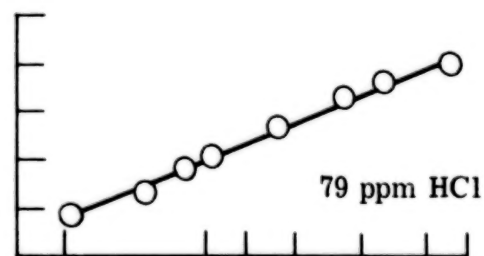
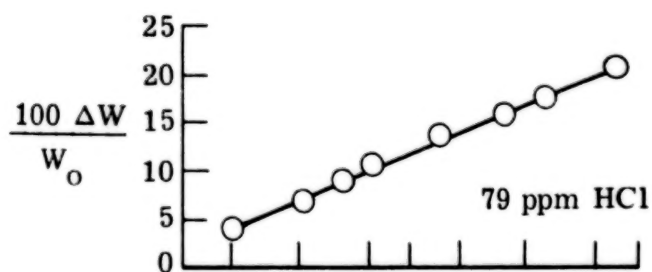
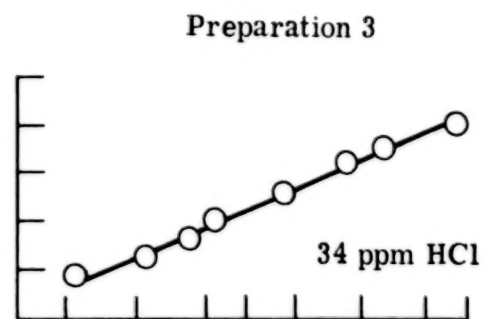
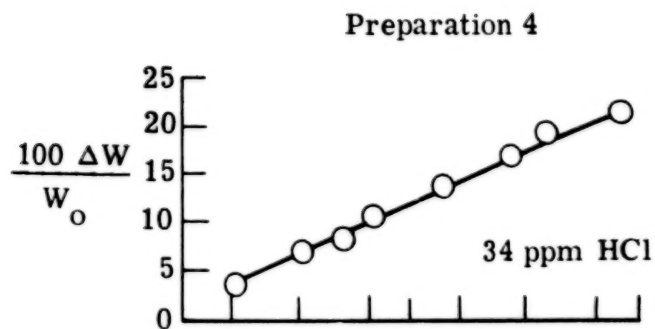
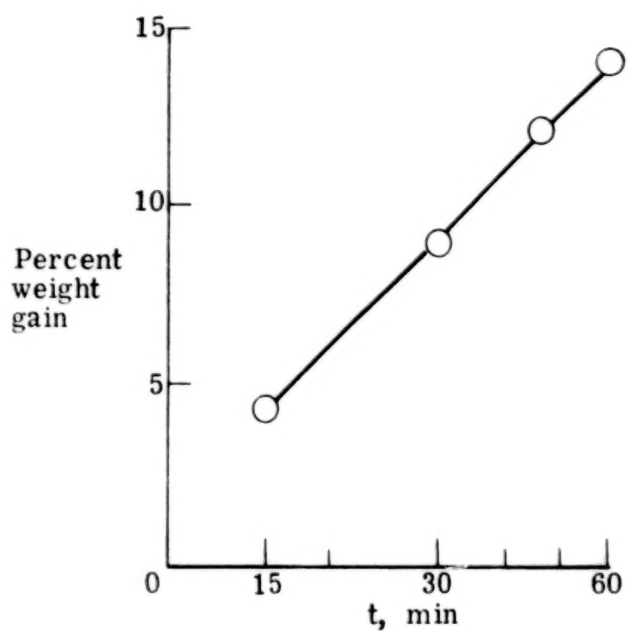
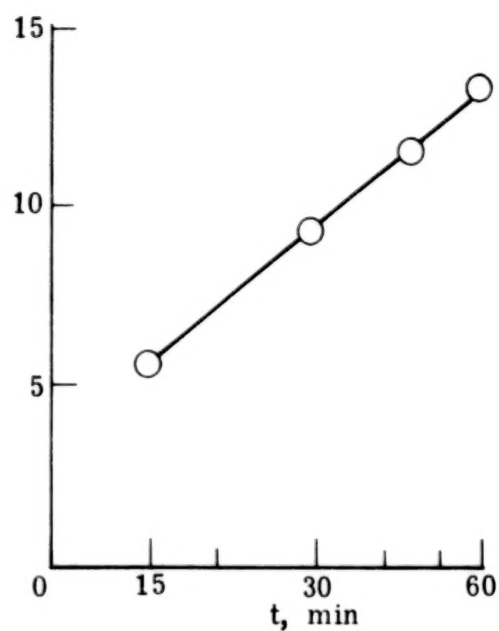


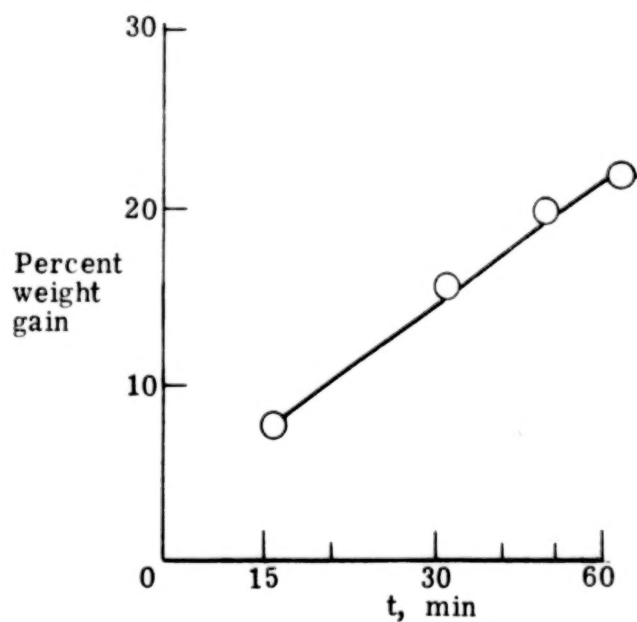
Figure 9.- Log-of-time fit for samples of preparations 3 and 4 exposed to different gaseous HCl concentrations.



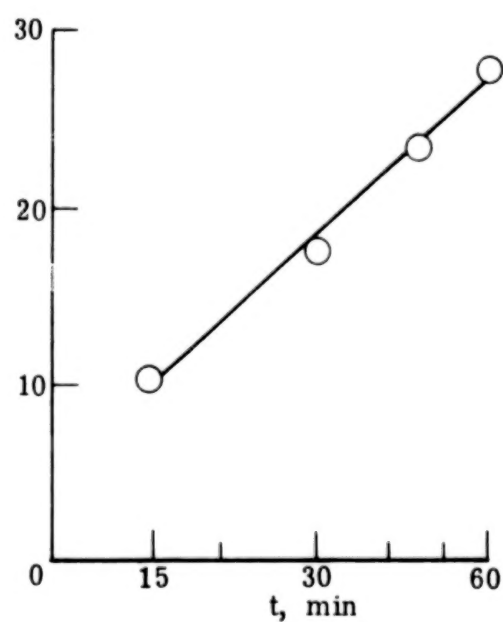
(a) No. 3, 79 ppm HCl.



(b) No. 4, 79 ppm HCl.

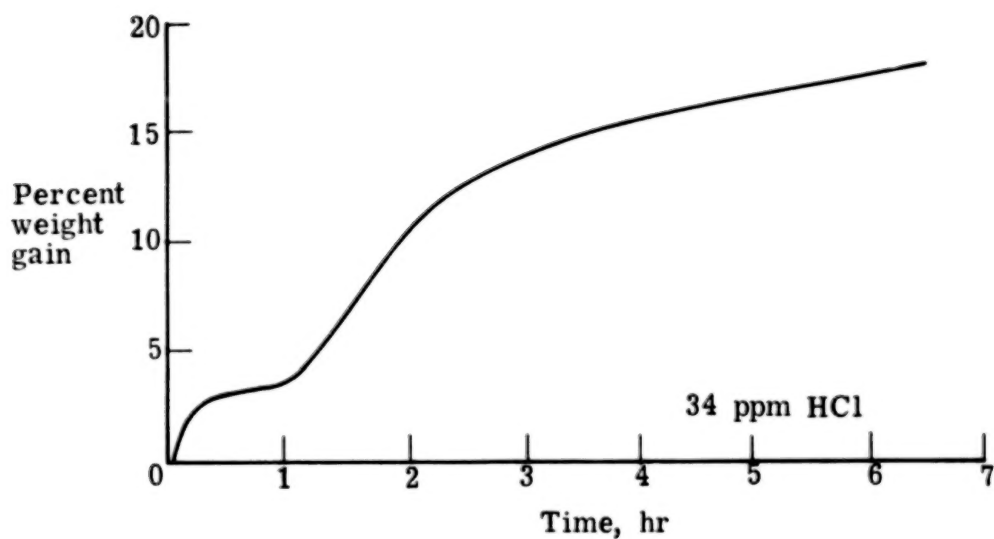


(c) No. 6, 79 ppm HCl.

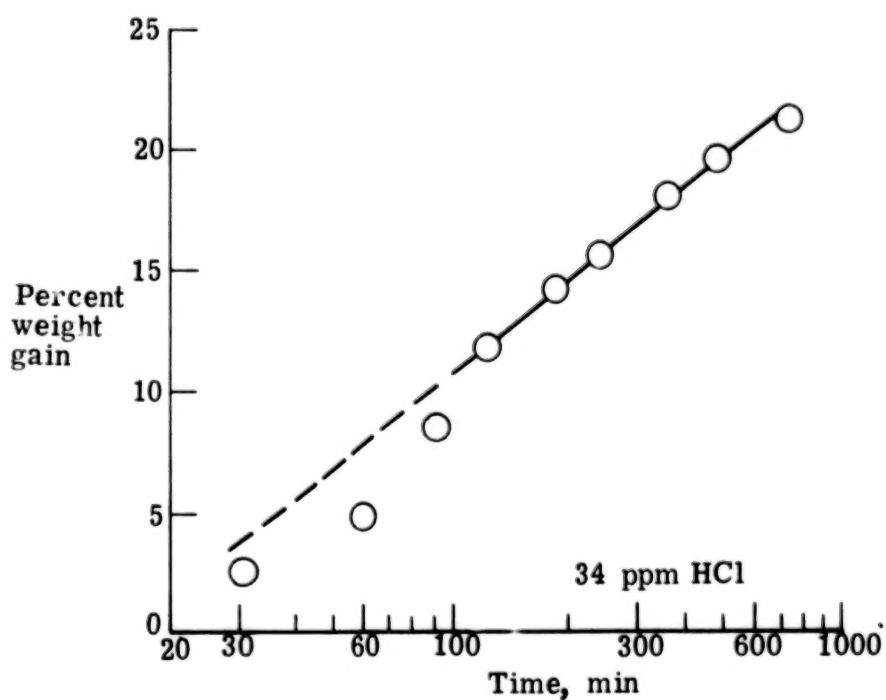


(d) No. 8, 79 ppm HCl.

Figure 10.- First-hour log-of-time fit for metastable aluminas.



(a) Real-time relationship.



(b) Log-of-time relationship.

Figure 11.- Sorption history displaying early plateauing.

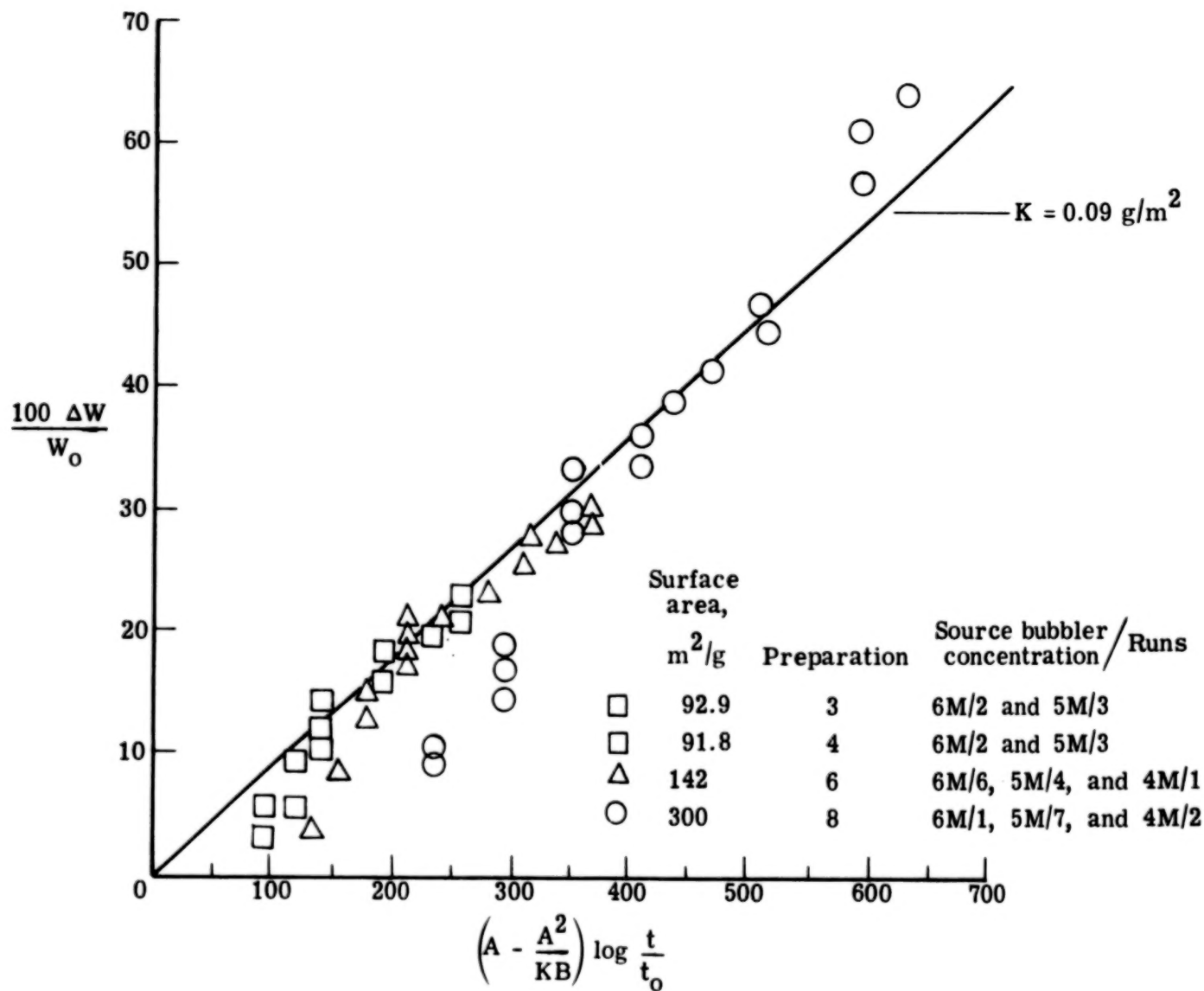


Figure 12.- Data fit of empirical correlation.

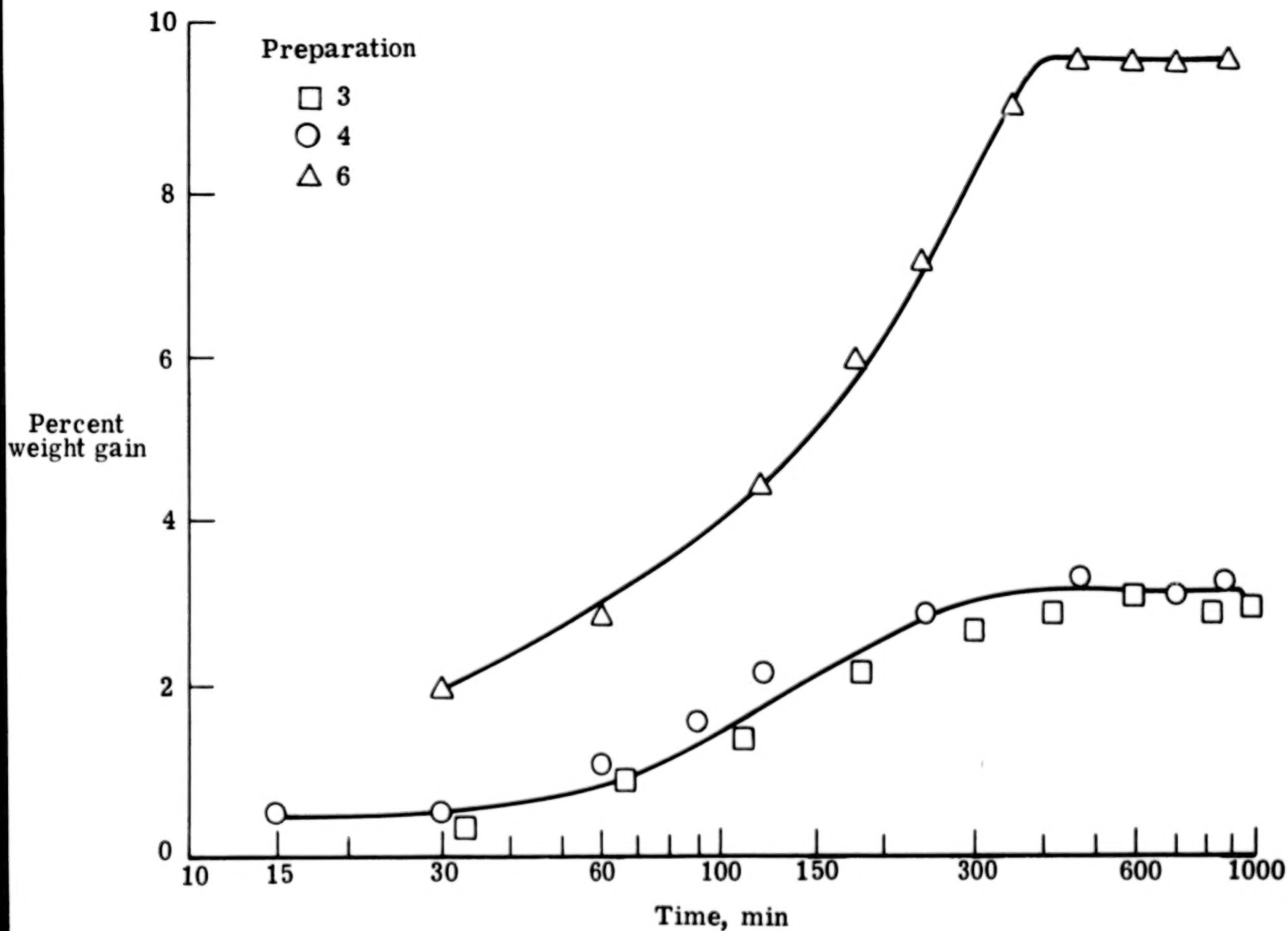


Figure 13.- Log-of-time fit for water sorption.

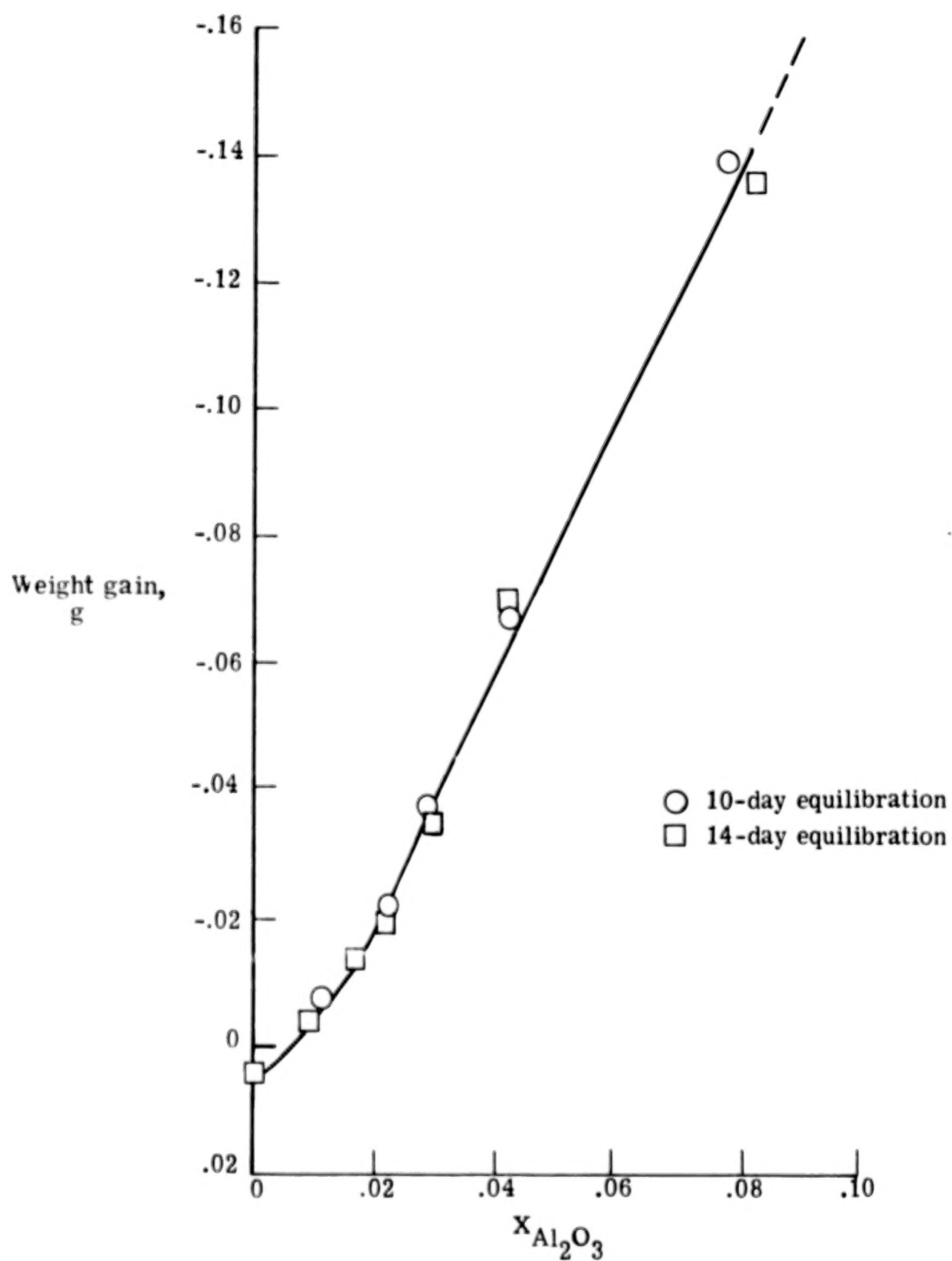
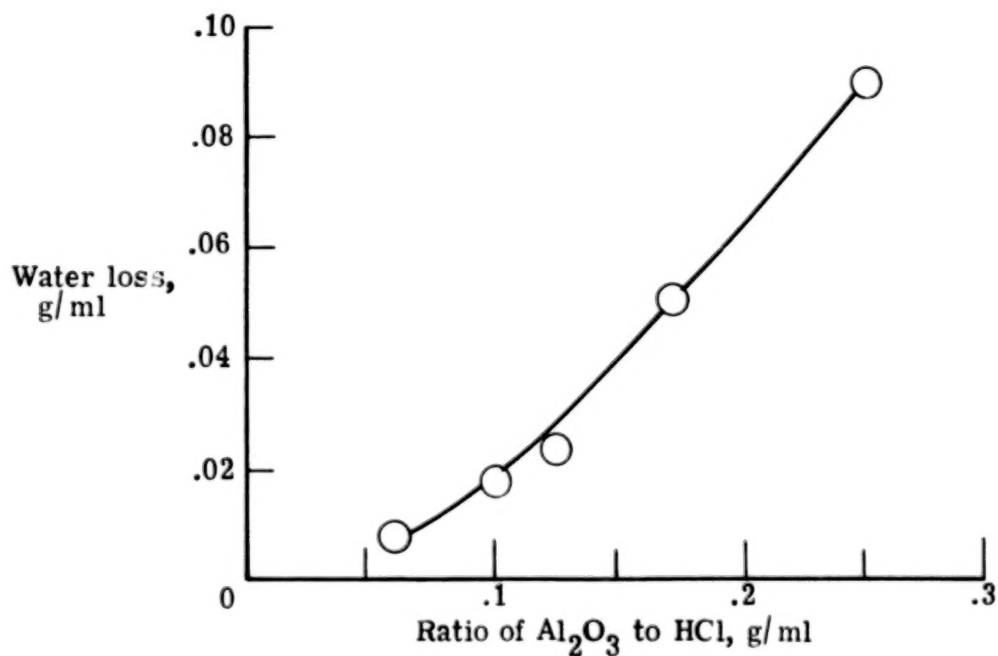
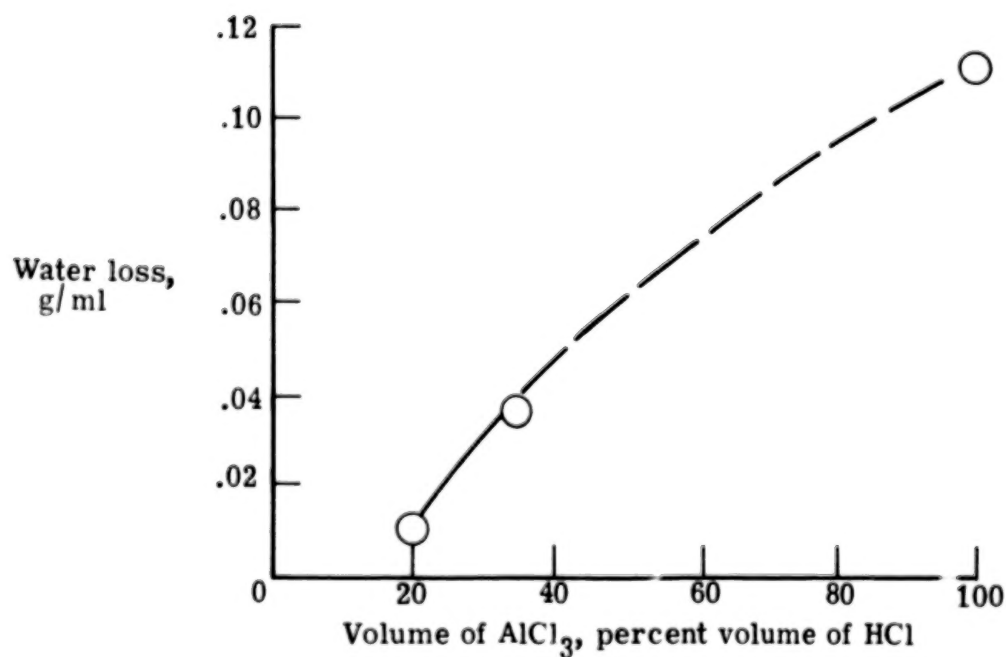


Figure 14.- Weight gains of  $\text{HCl}/\text{H}_2\text{O}/\text{Al}_2\text{O}_3$  mixtures equilibrated with hydrochloric acid reservoir.



(a) Mixtures of  $\text{HCl}/\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ .



(b) Solutions of aluminum chloride in hydrochloric acid.

Figure 15.- Isopiestic water loss.

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16. Abstract  <p>Hydrogen chloride (HCl) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) are major exhaust products of solid rocket motors (SRM). An understanding of the interaction of HCl with Al<sub>2</sub>O<sub>3</sub> in the presence of H<sub>2</sub>O is important in an environmental impact assessment. Samples of calcination-produced alumina were exposed to continuously flowing mixtures of gaseous HCl/H<sub>2</sub>O in nitrogen. A continuously recording microbalance measured weight gains throughout sorption histories. Transient sorption rates, as well as maximum sorptive capacities, were found to be largely controlled by specific surface area for samples of alpha, theta, and gamma alumina. Sorption rates for small samples were characterized linearly with an empirical relationship that accounted for specific area and logarithmic time. Chemisorption occurred on all aluminas studied and appeared to form from the sorption of about a 2/5 HCl-to-H<sub>2</sub>O mole ratio. The chemisorbed phase was predominately water soluble, yielding chloride/aluminum III ion mole ratios of about 3.3/1 suggestive of dissolved surface chlorides and/or oxychlorides. Isopiestic experiments in hydrochloric acid indicated that dissolution of alumina led to an increase in water-vapor pressure. Dissolution in aqueous SRM acid aerosol droplets, therefore, might be expected to promote evaporation.</p>					
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